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SUPPLEMENT TO MELLOR'S COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME V

PART BI: BORON–HYDROGEN COMPOUNDS

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

By J. W. Mellor, D.Sc., F.R.S.

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QD
31
.M52
Vol. 5
Suppl.
pt. B1

Supplement to

MELLOR'S COMPREHENSIVE
TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

Prepared under the direction
of an Editorial Board

VOLUME V

Boron

Part BI: Boron–Hydrogen Compounds

LONGMAN
London and New York

cm 5/6/82

Longman Group Limited
Longman House
Burnt Mill, Harlow, Essex, UK
Published in the United States of America
by Longman Inc., New York

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First published 1981

British Library Cataloguing in Publication Data

Mellor, J. W.
A comprehensive treatise on inorganic and theoretical chemistry
Vol. 5
Supplement 1 : Boron
Part B1 : Boron-Hydrogen compounds
1. Chemistry, Inorganic
I. Title
546 QD151.2 79–40162

ISBN 0-582-46278-9

The Library of Congress has catalogued this serial publication as follows:

Mellor, Joseph William, 1873–1938.

A comprehensive treatise on inorganic and theoretical chemistry. London, New York, Longmans, Green, 1922–[37]
Includes bibliographies.
—— ———— Supplement.
London, New York, Longman's, Green,
1. Chemistry, Inorganic. 2. Chemistry, Physical and theoretical.
QD31.M52 540 22–7753

Typeset, printed and bound in Great Britain by William Clowes (Beccles) Limited, Beccles and London.

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PREFACE

This second Supplement to Volume V follows Part A, Boron–Oxygen Compounds, which was published in 1980. As stated therein, the sheer mass of relevant literature developed since the original Volume V appeared in 1924 necessitated not only a separate volume for "Boron", but also that the Supplement be divided into separate parts. It was originally intended that Part B should cover boron–hydrogen, boron–halogen and related compounds but further sub-division has been found necessary. Accordingly, this volume is devoted very largely to the boranes and their derivatives. Boron–halogen compounds will be included in BII.

The publishers have been fortunate in continuing to retain the services of the specialist editor, Professor Raymond Thompson, Managing Director of Borax Research Limited. The general editing of this Supplement has again been the responsibility of Miss Bobbi Gouge of Longman, and her efforts are once more acknowledged.

There is inevitable delay between the publication of original papers and their careful consideration and compilation into a comprehensive review. Authors also complete their contributions at different times. As with Part A, cut-off dates of the literature used are given for each Section. Chemical Abstracts reference numbers have again been included, and the coverage spans the half-century or so between the publication of the original Volume and the availability of computerised access to this type of reference.

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ABBREVIATIONS

absolute	abs.
alternating current	a.c.
ampère-s	amp
Angstrom unit-s	Å
atmosphere-s (after a numeral)	atm
atomic weight	at. wt
boiling point	b.p.
British thermal unit-s	B.Th.U.
Calorie-s (large)	kcal
calorie-s (small)	g-cal
centimetre-s	cm
cubic centimetre-s	cm^3
density (with a numeral)	ρ, *d*
direct current	d.c.
electromotive force	e.m.f.
foot, feet	ft
freezing point	f.p.
gram-s (with a numeral)	g
hour-s (with a numeral)	hr
inch-es	in.
kilogram-s	kg
kilowatt-s	kW
litre-s (with a numeral)	l
melting point	m.p.
milliampère-s	mA
millilitre-s	ml
millivolt-s	mV
minute-s	min
molecular weight	mol. wt
parts per million	p.p.m.
potential difference	p.d.
second-s (time only)	s
specific gravity	sp. gr.
square centimetre-s	cm^2
vapour density	v.d.
vapour pressure	v.p.
volt-s	V
watt-s	W
wave-length	λ

Abbreviations of Journal titles, etc., in references are listed in Volume VIII, Supplement 1, Nitrogen (Part I), pp. xi–lxviii. A few additional abbreviations have unavoidably been introduced; these conform to current practice in 'Chemical Abstracts'.

SECTION B1

MONOBORANES AND ADDUCTS OF BORANE(3)

BY L. H. LONG

INTRODUCTION

None of the monoboranes can be isolated under ordinary conditions of temperature and pressure. In fact, of the smaller boranes (or boron hydrides) containing up to 3 boron atoms, only one—diborane(6)—is isolable. The rest are either short-lived molecules or molecular fragments. Nevertheless, the transitory existence of some of them is of crucial importance from the mechanistic point of view, and this importance is not confined to the subject of borane interconversions. Moreover, a number of these fleeting fragments form stable derivatives, which also require treatment.

The present section deals with all the known monoboranes, neutral and charged, along with their more important simple derivatives, except that the very numerous and important substituted derivatives of borane(3) BH_3 are treated elsewhere in these volumes and only the adducts are included here. (For the substituted derivatives of BH_3, see Section B7 p. 399; also Part A, p. 703 and Part BII Sections B11 and B13.) Separate sections are devoted to diboranes, triboranes, tetraboranes and higher boranes.

The nomenclature adopted for neutral species is that now in common use, namely to provide the borane with a prefix to denote the number of boron atoms in the molecule or radical (the prefix 'mono' is frequently omitted) and with a parenthetic arabic numeral as suffix to denote the number of hydrogen atoms. For ions of a very transitory nature usually encountered only in the mass spectrograph a similar nomenclature followed by the words 'positive ion' or 'negative ion' is preferred on the rare occasions when it is desired to name them; but for stable or relatively long-lived anions known in solution—and frequently in the solid state as well—the term 'hydroborate anion', with suitable prefixes to denote number of hydrogen and boron atoms and with the charge in parentheses as suffix, is used. (Among the lighter boranes, no true long-lived simple cations are known, although more complex coordinated species exist.) Thus:

B_2H_6 = diborane(6); B_4H_{10} = tetraborane(10);
BH_3^+ = borane(3) positive ion;
B_2H^- = diborane(1) negative ion;
$B_3H_8^-$ = octahydrotriborate(1–) anion.

But it is also common practice to refer to the species merely by their formulae, especially in the case of charged molecular fragments.

BORANE(1), BH, AND THE IONS BH^+ AND BH^-

The diatomic species BH, borane(1), has long been known from its spectrum. The ground state is $^1\Sigma^+$, and several excited states have been recognized. Emission lines of BH can be produced from a mixture of hydrogen and boron trichloride in the electric discharge tube.[1–2] Momentary concentrations can be high enough to obtain an absorption spectrum[3], and such has also been obtained from the front of a reflected shock wave in a BCl_3-H_2 mixture.[4] In addition, the absorption spectra of both BH and deuteroborane(1) BD have been obtained from flash photolysis experiments with borane carbonyl[5–6] and diborane.[7] Moreover, lines due to BH have also been observed in spectra of sun-spots, but not of the solar disc.[8–9]

The production of BH has also been observed in the fragmentation of B_2H_6 behind shock-wave fronts[10], in the pyrolysis of diborane at high temperatures and exceedingly low pressures[11], and in the high-temperature reaction of hydrogen with boron carbide.[12] (In the last two cases the formation of BH was demonstrated mass-spectrometrically.) The species is also one of those detected in burning diborane[13], and its transition probabilities in flames have been calculated.[14]

Spectroscopic and, to a lesser extent, electron-impact studies have provided considerable information about this molecule. Many spectroscopic constants for the ground state and several excited states of BH and BD were originally tabulated by Herzberg[15] but have since been partly revised.[5–6] What is known concerning the ionization potential[5], internuclear distance[5], stretching force constant[16], and dissociation energy[6, 17–18] of BH is listed in Table I. In addition, for the lowest triplet excited level,

Table I.—Miscellaneous Molecular Properties of Some Monoborane Species in Their Ground States

Species BH_n or BH_n^+	Ionization potential (eV)	Dissociation energy $D(\mathrm{H}_{n-1}\overset{(+)}{\mathrm{B}}\text{—H})$ (eV)	r(B—H) (Å)	Interbond angle	Stretching force constant (mdyn Å^{-1})	Dipole moment (D)
BH	9·77 ± 0·05(a) 9·73 ± 0·01(e)	< 3·58(b) > 3·38(f) 3·64(h) 3·58 (D_e)(e)	1·236 (r_e)(a)	—	3·032(c) 3·044(g)	1·27 ± 0·21(d)
BH^+		< 2·11(a) 2·17(h)	1·2146 (r_e)(i)	—		
BH_2	*c.* 9·37(h)	*c.* 3·90(h)	1·181 (r_0)(j)	131°(j)		
BH_2^+		0·80(k) 0·71(l) 0·89(m)				
BH_3	12·32 ± 0·1(h,k)	*c.* 3·58(h)		120°(n)	4·08(o)	
BH_3^+		0·63(h) 0·66(k)				
BH_4		< 1·81(p)				

(a) Ref. 5. The value for $D(B^+\text{—}H)$ has been corrected for revised predissociation data in Ref. 6.
(b) From predissociation data in Ref. 6.
(c) From results in Ref. 5 as calculated in Ref. 16.
(d) Ref. 19.
(e) Calculated in Ref. 20 from experimental data and annotations compiled in Ref. 21.
(f) The lower limit of Ref. 17 raised by 0·03 eV, as required by the results of Ref. 6.
(g) Cited in Ref. 20 from an unpublished compilation of Mulliken & Ramsay.
(h) Ref. 18.
(i) Ref. 15.
(j) Ref. 22.
(k) Ref. 23.
(l) Derived from the difference in the appearance potentials of BH^+ and BH_2^+ from BH_3 reported in Ref. 18. The much higher value (4·30 eV) cited in the same paper is now withdrawn as erroneous (Ref. 24).
(m) Derived from the difference in the appearance potentials of BH^+ and BH_2^+ from B_2H_6 reported in Ref. 18.
(n) Assumed symmetry D_{3h} in Ref. 25.
(o) Ref. 25.
(p) This quantity will be less than $D(CH_3^+\text{—}H)$ for the isoelectronic species CH_4^+, the value for which is close to 1·81 eV as derived from $D(CH_3\text{—}H)$ [4·477 ± 0·005 eV, Ref. 26] plus the ionization potential of CH_3 [9·843 ± 0·001 eV, Ref. 27] minus the ionization potential of CH_4 [*c.* 12·51 eV, Ref. 28].

the $a\,{}^3\Pi_r$ state, the spin-orbit coupling constant A (5·95 cm^{-1}) has been derived spectroscopically[15]; while the dipole moment has been determined at 1·27 ± 0·21 D for the ground state and 0·58 ± 0·04 D for the excited $A\ {}^1\Pi$ state from the observed Stark effect in a strong electric field.[19] The enthalpy of formation and other thermodynamic data for BH gas in its ideal state at 0 and 298·15 K have been listed in a compilation[29] and are reproduced in Table II. A tabulation covering a wider temperature range is also available.[30] (Discrepancies between the compilations arise in part from different arbitrary weightings of rather inaccurate source data.)

Largely because with only six electrons the BH molecule happens to be one of the simplest molecules possible (and in fact the simplest uncharged molecule derived from an atom with a *p* electron), it has been the subject of an exceptionally large amount of theoretical treatment by many workers, of which only a few can be mentioned. Thus semi-empirical methods have been used to predict values for the electron affinities of two ideally hybridized states of BH (0·08 and 0·42 eV respectively)[34–5], and the nature and positions of the lower electronic levels.[36] Use has been made of an internuclear potential function to calculate a number of parameters for the ground states and a few excited states of BH and BD.[37] The potential-energy curve of the ground state of BH has been calculated[38], while a computation of the Franck–Condon factors and *r* centroids of the bands has been undertaken to explain the intensity distribution in the *A-X* band system.[39] Another theoretical prediction is based on perturbed Hartree–Fock calculations, namely that BH in its ground state while possessing no unpaired electrons should manifest a weak temperature-independent paramagnetism[40–2], a conclusion that has been supported in measure by other arguments of a theoretical nature.[43] The cause of this predicted paramagnetism is attributed to the perturbing effect of the lowest unoccupied π orbital on the orbital housing the lone pair of electrons, which is tantamount to a measure of promotion of this electron pair and gives rise to an induced paramagnetic current that is much more than large enough to swamp the small underlying diamagnetism. The associated large negative rotational magnetic moment would appear to imply that in molecular rotation the rotation of the electron cloud completely dominates over that of the nuclei.[41] Moreover, the treatment also predicts that the boron atom is antishielded and has a spin rotation constant larger than any previously observed. The BH molecule may therefore justly be claimed as one of exceptional interest. A separate Hartree–Fock treatment of the ground state has been published in a paper which also provides a useful summary of the results of earlier theoretical work.[20] Somewhat more recent and in part improved treatments, some of them including electron correlation, have been based on a separated pair approximation[44], configuration interaction[45–7], a molecular orbital approach adopting a localization procedure[48], generalized valence bond wave functions[49], the so-called GI and SOGI (spin-coupling optimized GI) methods[50], semi-empirical effective pair correlation[51], independent pair-potential correlated wave functions[52], and various *ab initio* procedures.[53–6] The last treatment indicates that the bonding on the boron atom of BH is almost pure *p*.[56] Most recently, other refined and sophisticated treatments of the molecule have been undertaken[47, 57–71], including a computation of the charge distribution and multiple moment on various theoretical bases.[72]

For reactions involving BH little is known. It has been postulated as an intermediate in the radiolysis of pentaborane(9).[73] Activation energies, frequency factors and rate constants have been computed for hydrogen-transfer to and from other light atoms[74], and for the reaction forming 2BH from $BH_2 + B$.[75]

The ionized species BH^+ is isoelectronic with BeH, an elusive radical known only from its spectrum. Although spectral lines due to BH^+ are frequently produced[2] along with those due to BH, much less is known about the ionized species, particularly about its excited states. BH^+ is also observed in the mass spectra of boranes[76–80], as is its deuterated analogue BD^+.[79, 81–2] Their appearance potentials from diborane are given in Table III. The ground state is ${}^2\Sigma^+$ and some molecular parameters are given in Table I. Although the B—H internuclear distance is slightly less than for neutral BH, thus implying slightly stronger bonding, the dissociation energy (to $B^+ + H$) is appreciably lower.[5, 18] The nature of the bonding has been considered.[86] The spin-orbit

Table II.—Calculated Thermodynamic Data for the Formation of Some Borane Species[29]

Species	State	ΔH°_f	ΔH°_f	ΔG°_f	$H^\circ_{298\cdot15}-H^\circ_0$	S°	C_p°
		kJ mol^{-1} (kcal mol^{-1})				J mol^{-1} K^{-1} (cal mol^{-1} K^{-1})	
		0 K	298·15 K				
BH	g	446·4 (106·7)	449·61 (107·46)	419·61 (100·29)	8·640 (2·065)	171·75 (41·05)	29·16 (6·97)
BH_3	g		100[(a)] (24)[(a)]				
BH_4^-	H_2O soln [(b)]		48·16 (11·51)	114·27 (27·31)		110·5 (26·4)	
B_2H_6	g	51·42 (12·29)	35·6 (8·5)	86·6 (20·7)	11·954 (2·857)	232·00 (55·45)	56·90 (13·60)
	n-C_5H_{12} soln[(c)]		25·1 (6·0)	96·2 (23·0)		164·8 (39·4)	
B_4H_{10}	g		66·1 (15·8)				
B_5H_9	cryst	57·011 (13·626)					
	l		42·68 (10·20)	171·67 (41·03)	29·836 (7·131)	184·22 (44·03)	151·13 (36·12)
	g	102·09 (24·40)	73·2 (17·5)	174·9 (41·8)	15·322 (3·662)	275·81 (65·92)	96·78 (23·13)
B_6H_{10}	l		56·27 (13·45)				
	g		94·6 (22·6)				
$B_{10}H_{14}$	cryst	−2·075 (−0·496)	−45·2 (−10·8)	192·0 (45·9)	28·292 (6·762)	176·57 (42·20)	217·94 (52·09)
	g	78·111 (18·669)	31·55 (7·54)	216·15 (51·66)	24·845 (5·938)	353·1 (84·4)	179·66 (42·94)

(a) This figure from Ref. 29 rests on an assumed value for $D(H_3B\cdots BH_3)$ which is known to be highly dubious. The corresponding figure in Ref. 30 is 107 ± 42 kJ mol^{-1} (25·5 ± 10 kcal mol^{-1}), while that in Ref. 31 is 144 ± 8 kJ mol^{-1} (34·5 ± 2 kcal mol^{-1}), the last value being derived from mass-spectrographic work and the assumption that BH_3 can be produced from B_2H_6 with zero or negligible kinetic energy, that is, that there is no appreciable energy barrier for the interaction of two BH_3 molecules. Yet another value can be derived from the equilibrium studies with $B_2H_2Me_4$ of Ref. 32 combined with the estimated entropy values of substituted boranes and diboranes of Ref. 33, namely the very approximate value 64 kJ mol^{-1} (15·2 kcal mol^{-1}).

(b) Hypothetical ideal solution of unit molality.

(c) Hypothetical ideal solution of unit mole fraction of solute.

Table III.—*Appearance Potentials of Monoborane Positive Ions from Borane(3), Diborane(6) and Hexadeuterodiborane(6)*

Parent borane / Ion	Appearance potential of ion (eV)						
	BH_3			B_2H_6			B_2D_6
	Ref. 83	Ref. 18	Ref. 23	Ref. 84	Ref. 85	Ref. 18	Ref. 85
$^{10}BH_3{}^+$, $^{10}BD_3{}^+$				12·1 ± 0·2	13·1 ± 0·2		12·7 ± 0·2
$^{11}BH_3{}^+$	11·4 ± 0·2	12·32 ± 0·1	12·24 ± 0·1			14·88 ± 0·05	
$^{10}BH_2{}^+$, $^{10}BD_2{}^+$		12·95 ± 0·05		13·5 ± 0·2	13·4 ± 0·1	15·50 ± 0·05	13·6 ± 0·1
$^{11}BH_2{}^+$				12·0 ± 1·0			
$^{10}BH^+$, $^{10}BD^+$		13·66 ± 0·02		16·6 ± 0·2	14·9 ± 0·1	16·39 ± 0·3	14·8 ± 0·1
$^{10}B^+$		15·83		19·2 ± 0·2	18·7 ± 0·1	18·39 ± 0·02	18·6 ± 0·1
$^{11}B^+$				20·1 ± 0·5			

coupling constant of the excited $A\ ^2\Pi$ state (14·0 cm^{-1}) has been calculated from spectroscopic data[15] and from theoretical approaches.[87–9, 63] The potential-energy curves of the ground and first excited states have also been derived theoretically.[38, 66]

The negative ion BH^- has been encountered only in the mass spectrometer, and can be detected in the negative-ion mass spectra of diborane(6) and pentoborane(9).[90] On the basis that it is isoelectronic with CH, the ground state is $^2\Pi$, and several excited states have been predicted, for all of which the valence-state energies of the B^- charged atomic species have been calculated.[91] The potential-energy curve of the $^2\Pi$ state has been calculated.[66]

BORANE(2), BH_2, AND THE IONS BH_2^+ AND BH_2^-

Conclusive evidence for the existence of neutral BH_2 (borane(2), or the boryl radical) was first reported in 1967 with the publication of its absorption spectrum obtained during flash photolysis experiments with borane carbonyl.[22] Lines due to $^{10}BH_2$ and $^{11}BD_2$ have also been observed and the electronic and geometric structures of the lowest states have been determined. In the ground ($X\ ^2A_1$) state the molecule is bent, a structure long predicted.[92–3] The angle at the boron atom is 131° [22, 94], to be compared with values in the range 136°–144° for other dihydride species of first-row elements containing only one electron in the in-plane 'pi' orbital.[95] Trigonal hybridization of the boron in BH_2 reportedly requires 7 kcal mol^{-1} less promotional energy than digonal.[34] A known excited state, $A\ ^2B_1(\Pi_u)$, is linear[96, 94], however, and the effect of quasi-linearity on the anharmonicities of the bending vibrations has been calculated.[97] Earlier it had been claimed that neutral BH_2 is produced in the pyrolysis of diborane(6)[83], but later, very careful work appears to have refuted this[18], and for energetic reasons, it must be concluded that it is in any case unlikely.[98] This, however, does not exclude its formation in photodecomposition, and BH_2 has been assumed to be formed in the primary step in photolysis of diborane(6) sensitized by hexafluoroacetone.[99] It has also been claimed (surprisingly) as a product of a metastable transition in the gas phase, namely

$$B_4H_9^+ \rightarrow B_3H_7^+ + BH_2$$

which was thought to occur during mass-spectral experiments with tetraborane(10).[100] Unlike BH and BH_3, BH_2 is apparently not formed in the high-temperature reaction of hydrogen with boron carbide[12], but it may have been observed in an argon matrix containing the products of the $B+H_2$ reaction by e.s.r. studies below 10 K.[101] The ionization potential of BH_2 has been established[18], as have the B—H interatomic distance[22] and the dissociation energy D(HB—H).[18, 23] The values are listed in Table I. A computed table of thermodynamic values[30] is of very little value for this species because of inaccurate and (in part) erroneous source data.

Theoretical treatments have dealt with such matters as the calculation of the electronic levels[36] and their potential-energy curves[102] and bond dissociation energies[103], the ionization potential of the ground state[103, 70], the electron affinity[34] and the stretching and bending force constants[70], while others consider the geometry[50, 104–5] and the unpaired spin distribution[104], the last by a new approximate self-consistent-field method. Agreement with experiment, where this can be tested, is only occasionally better than fair, the first treatment even incorrectly predicting a linear ground state. Substantially better agreement has more recently been obtained for a wide variety of molecular parameters with *ab initio* calculations (without and with electron correlation) for both the ground and first excited states.[56, 106–8] A large disagreement, however remains in the case of the transition energy between the states, and this has led the authors to claim[106–7] that (exceptionally) the theoretical value is nearer the truth, and that the spectroscopic value[22] rests on an incorrect numbering of the vibrational levels.

Nothing is known about the reactions of BH_2, but the activation energy and frequency factor for the process

$$BH_2 + B \rightarrow 2BH$$

have been calculated.[75]

The BH_2^+ positive ion is known from the mass spectra of boranes[76–80], as is also BD_2^+.[79,81–2] It has been claimed that BH_2^+ exists as a cation in aqueous solution[109], but that is only likely if the boron is coordinated with water molecules, e.g., as the ionic species $[BH_2(OH_2)_2]^+$, which would greatly modify the hydridic character of the hydrogen atoms. Mass-spectrometric studies[18,23] have led to a value for $D(HB^+\text{—}H)$ (see Table I). The structure of the BH_2^+ molecule-ion has been predicted to be linear[92–3], a conclusion which is supported by theoretical treatments of a more sophisticated nature.[105,110–14] The predicted B—H bond length[114] is almost identical with that for neutral BH_2.

A derivative of BH_2^+ is the positive ion BMe_2^+, which is known from ion cyclotron resonance spectroscopy.[115]

The negative ion BH_2^- is known only from the negative mass spectra of diborane(6) and pentaborane(9).[116,90] The molecule, which is isoelectronic with methylene CH_2, should have a bent structure[105], and the angle would be expected to be smaller than in neutral BH_2. A recent calculation predicts an angle of 102° for BH_2^-.[117] The B^- valence states[34] and valence-state energies[91] for various hypothetical states of BH_2^- have been derived.

A derivative of BH_2^- is the anion $B(n\text{-}Bu)_2^-$, which is known as its potassium salt $KB(n\text{-}Bu)_2$, prepared by treating chlorodi-*n*-butylborane with sodium-potassium alloy[118–19]:

$$B(n\text{-}Bu)_2Cl + 2K \rightarrow KB(n\text{-}Bu)_2 + KCl$$

BORANE(3), BH_3

Detection and Formation

Until 1964, all attempts to observe borane(3) BH_3 failed, and it has still never been observed in true equilibrium with its dimer, diborane(6). Because it has never been formed in the absence of B_2H_6 or some other compound with which it instantly reacts, the production and detection of even trace amounts of BH_3 is fraught with difficulties. Its presence was apparently first demonstrated experimentally about the same time by R. W. Diesen in unpublished work on reactions behind shock-wave fronts—presumably in diborane(6)—and referred to in the work of others[120], and by two independent groups of workers[83,121,11] investigating the high-temperature pyrolysis of B_2H_6 at very low pressures (i.e. below the bimolecular region). Identification in all these cases depended on mass-spectrometric evidence. The pyrolysis process is highly inefficient (2–3%[11]) and has been ascribed to a wall reaction.[122] For this the energy of activation is *c.* 26 kcal mol^{-1}, much lower than that for the homogeneous process $B_2H_6 \rightarrow 2BH_3$, which has been measured at 59 kcal mol^{-1} [18,23] (including any potential barrier to be surmounted during dissociation). This high value makes intelligible the preferential decomposition of diborane by an alternative route in the bimolecular pressure region[98], namely

$$2B_2H_6 \rightarrow BH_3 + B_3H_9$$

which is energetically more favourable and takes place at a much lower temperature. Accordingly a different source of BH_3 is preferable, and the pyrolysis of borane carbonyl BH_3CO has been found to be suitable.[123] Diluted with an inert carrier gas, it can give an initial yield of up to 60% of BH_3.[124] It is known from an interpretation of accumulated experimental evidence[98] that BH_3 is also split off as a unit in the decomposition of certain higher boranes, namely B_4H_{10}, B_5H_{11}, B_6H_{12} and n-B_9H_{15}, and in some cases confirmation is forthcoming from molecular-beam mass spectra of boranes pyrolyzing at or above 100°C.[125] Finally, along with BH, borane(3) has also been identified as a product of the high-temperature reaction of hydrogen with boron carbide.[12]

The detection of BH_3 is thus now well established, but many attempts to isolate it, even at the temperature of liquid nitrogen, failed. Borane(3) is spontaneously converted to diborane(6)—though the route is more complex than simple dimerization (p. 9) even at pressures as low as 10^{-5} Torr, and it has been concluded that the isolation of borane(3) at 77 K is unlikely, though traces will survive condensation and revaporization at 65–67 K.[31] Only under difficult and narrowly restricted conditions below 35 K has it proved feasible to trap BH_3 (and possibly trideuteroborane(3) BD_3) for a limited time at a concentration of $<0{\cdot}1\%$ in an argon matrix.[25]

Molecular and Physical Properties

By means of the argon-matrix technique the infra-red spectra of BH_3 and some isotopic analogues, and hence their fundamental vibrational frequencies (Table IV), have

Table IV.—Observed Vibrational Frequencies of Borane(3) and Isotopic Species[25]

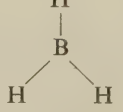
Fundamental	Frequency (cm^{-1})		
	$^{11}BH_3$	$^{10}BH_3$	$^{11}BD_3$
$\nu_1(A_1')$	(2623)[(a)]		
$\nu_2(A_2'')$	1125	1132	845
$\nu_3(E')$	2808	2820	(2118)[(b)]
$\nu_4(E')$	1604	1610	(1172)[(b)]

(a) Infra-red-inactive. The value is predicted.
(b) Predicted value from force-constant calculations.

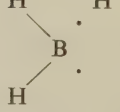
been obtained for the first time.[25] The observed bands are at quite different positions from those reported earlier for short-lived products from pyrolyzing diborane(6)[126–8], which suggests that in the earlier work some other transitory borane species (such as B_3H_9, B_3H_7, or B_4H_8) and not BH_3 was being observed. From the latest set of wave numbers, force constants for the BH_3 molecule have been calculated[25], a planar structure being assumed. Virtually nothing else is known experimentally about the molecular properties, except the ionization potential and the bond dissociation energy $D(H_2B{—}H)$.[18, 23] Experimental values are listed in Table I. Non-experimental estimates for all the bond dissociation energies of the molecule had been obtained earlier by an interpolation procedure.[103]

Thermodynamic functions for BH_3 have been computed[30, 129–30], but they are unavoidably based on assumptions and, in any case, need recomputing for the latest spectroscopic and other experimental data. Likewise derived values for the enthalpy of formation have been published[29–31], but this quantity is related to the value for diborane(6) by the bridge-bond dissociation energy of the latter compound, which is uncertain. The values are reproduced in Table II (and footnote), but should be treated with the greatest reserve.

Even the structure of BH_3—which is isoelectronic with the oxygen atom—remains unestablished. Commonly it has been assumed or predicted to be



(I)



(II)

structure (I) with a planar geometry (point group D_{3h})[131, 36, 105, 110], but the possibility that it has the triplet structure (II) and is pyramidal has also found a measure of theoretical support.[132] A determination of the magnetic moment would decide the issue. The molecule has been the subject of numerous theoretical computations, including treatments based on a molecular self-consistent field[133], a fully optimized SCF wave function[134], equivalent orbitals[135], configuration interaction[136], a molecular-orbital set determined by a localization procedure[48], a floating spherical Gaussian orbital model[113], extended coupled-pair many-electron theory[137], CNDO and INDO semi-empirical methods[138-9], a formally charged valence-bond treatment involving orbital scaling[140], *ab initio* methods[56, 141-2] and other recent sophisticated procedures.[69-70, 143-6]

Chemical Properties

DIMERIZATION AND REACTIONS WITH OTHER BORANES

Contrary to older assumptions, there are good reasons for believing that the simple equilibrium

$$2BH_3 \rightleftharpoons B_2H_6$$

cannot be realized[98] and is hence of no significance in practical chemistry. The heat of dimerization of 2 moles of BH_3 is uncertain, being equivalent to the equilibrium bridge-bond dissociation energy of 1 mole of B_2H_6 (p. 64). But it has been predicted that a potential barrier[147] accompanies the simple dimerization of BH_3, and experimental evidence for this is presented in the section on diborane(6) (see p. 65). Difference between the results from equilibrium studies and mass-spectrometric studies provides experimental evidence that the height of this potential barrier is considerable[98], possibly of the order of 30 ± 10 kcal mol^{-1}. Such an additional energy barrier to dissociation would increase the stability of the B_2H_6 molecule and help to explain why its low-pressure pyrolysis process has the above-mentioned low efficiency (2–3%)[11] for the production of BH_3. The height of the potential barrier is difficult to calculate theoretically, but a recent treatment, while confirming that there is a barrier, has placed it a power of 10 lower, namely at 2·6 kcal mol^{-1}.[148] The cause of the discrepancy is not immediately apparent.

However, irrespective of the height of the barrier for simple dimerization, BH_3 can dimerize in other ways by steps that involve zero or exceedingly low activation energies, e.g.

$$BH_3 + B_2H_6 \rightarrow B_3H_9$$

followed by

$$BH_3 + B_3H_9 \rightarrow 2B_2H_6$$

or even

$$2B_3H_9 \rightarrow 3B_2H_6$$

Consequently, unless very special steps are taken to prevent it, BH_3 will disappear as soon as it is formed, and an attempt to measure the absolute rate of association of BH_3 with BH_3[149]—which incidentally provided a value (2×10^9 l mol^{-1} s^{-1} at 545 K) surprisingly close to the absolute rate of association of BH_3 with the very different molecule trimethylamine NMe_3[150] ($1{\cdot}1 \times 10^9$ l mol^{-1} s^{-1} at 500 K)—cannot compellingly be assigned to the assumed barrier-hindered process $2BH_3 \rightarrow B_2H_6$. Borane(3) has no unpaired electrons and the position is very different from that of the association of two CH_3 radicals to form a molecule of ethane, for which system not only is the interaction of the unpaired electrons attractive at all distances, but no comparable alternative paths of low activation energy exist.

Although it is such a transitory and elusive species, borane(3) has been known to react with many other borane species, and a summary of the evidence has been published.[98] Included are reactions such as

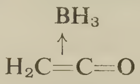
$$\begin{gathered} BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \\ BH_3 + B_3H_7 \rightleftharpoons B_4H_{10} \\ BH_3 + B_4H_{10} \rightleftharpoons B_5H_{11} + H_2 \\ BH_3 + B_8H_{12} \rightleftharpoons n\text{-}B_9H_{15} \end{gathered}$$

Such reactions are exothermic and very fast in the forward direction, possibly occurring at almost every collision. Specific study of such processes has only recently become possible, as in the cases of the direct interactions of BH_3 with diborane(6) and pentaborane(9) respectively.[151] These studies have been carried out so far at only one temperature (450 K), and the rate constants calculated are only very approximate; but the value obtained with B_2H_6 is about three times as large as that obtained with B_5H_9. The above-listed reactions forming and consuming BH_3 imply that BH_3 and its isotopic counterparts are key intermediates in deuterium-exchange reactions of diborane(6) with itself[152-3], with tetraborane(10)[154], and with pentaborane(11).[155-6] They are also believed to be intermediates in gas-phase exchange reactions of diborane with aluminium tetrahydroborate $Al(BH_4)_3$[157] and with μ-dimethylaminodiborane(6) μ-$B_2H_5NMe_2$[158] respectively.

REACTIONS WITH OTHER COMPOUNDS

Although many studies involving reactions with 'borane' in solution have been reported, such reactions are not necessarily reactions of free BH_3 but, rather, either those of dissolved B_2H_6 or those of adducts such as $H_3B.OC_4H_8$ (see pp. 36 and 126), or alternatively refer to still more complex species, and so do not concern us here. Thus the reductive cleavage of acetals in tetrahydrofuran solution is third-order in 'BH_3', suggesting that B_3H_9 is likely to be the active species in this instance.[159] Even where the reaction is first-order in BH_3, the rate-determining step in solution is almost certainly not one involving free BH_3. Reactions of the species in solution have been reviewed recently.[160]

The gas-phase reactions of free BH_3 with other classes of compounds have been relatively little studied to date, but what has been done is all due to the efforts of T. P. Fehlner and his collaborators[161], who have worked with helium as a carrier gas. In every case so far an addition is observed, but the addition products vary in type. The reactions also tend to be exceptionally fast. Hydroboration (p. 103) is to be expected with unsaturated carbon compounds, and this is indeed observed with ethylene, the initial product apparently being ethylborane.[162] The temperature dependence of the reaction rate implies an activation energy of *c.* 2 kcal mol^{-1}. With ketene $CH_2{=}C{=}O$ it is far less likely that hydroboration occurs as the initial step, although the product has the expected formula BC_2H_5O, while the rate constant is of the same order and again it is the carbon-carbon double bond which is attacked.[163] Even in the absence of proof of the final structure there is good reason for believing that the initial step involves donation of the π electrons of the $C{=}C$ bond to the boron atom to give a hitherto unknown transition complex of structure



$$\begin{array}{c} BH_3 \\ \uparrow \\ H_2C{=}C{=}O \end{array}$$

With donors such as trimethylamine NMe_3 and phosphorus trifluoride PF_3, the addition complexes are of the expected type ($H_3B.NMe_3$ and $H_3B.PF_3$).[150] With alcohols ROH the oxygen atom acts as donor, in that the initial step is the adduct $H_3B.OHR$[164]; but this is followed (at least in the case of the adduct of 2-propanol) by the elimination of hydrogen to form H_2BOR and its disproportionation products. Likewise with acetone it is apparently again a lone electron pair on the oxygen atom which donates to give $Me_2CO.BH_3$ as initial product.[165]

Bimolecular rate constants of typical examples of the foregoing reactions are listed in Table V.

Table V.—Bimolecular Rate Constants of Free BH_3 in the Gas Phase in the Presence of an Inert Carrier Gas

Second reactant	Temperature (K)	Rate constant (l mol^{-1} s^{-1})	Reference
B_2H_6	450	*c.* 3×10^7	151
B_5H_9	450	*c.* 10^7	151
C_2H_4	430	2×10^9	162
CH_2CO	460	4×10^9	163
NMe_3	500	$1{\cdot}1\times10^9$	150
PF_3	500	$1{\cdot}5\times10^8$	150
Me_2CHOH	450	*c.* 10^8	164
Me_2CO	450	3×10^8	165

Although no simple direct-substitution reaction of BH_3 has so far been described, the number of known substituted derivatives of BH_3 prepared by other methods is legion. Accordingly separate sections are devoted to that area of chemistry (p. 399; also Part A p. 703 and Part BII Sections B11 and B13), and only the adducts of BH_3 will receive mention in the present section.

Adducts

GENERAL

In spite of the very fleeting character of free BH_3, it forms a large number of relatively stable adducts[166], in which the BH_3 group becomes pyramidal.[167] With the acceptor powers conferred on it by its vacant orbital, BH_3 is a strong Lewis acid, though in energetic terms its powers to form a simple adduct are reduced by half the energy of association of $2BH_3$ to diborane(6), which latter species is liable to be released if the donor or Lewis base with which it is linked is too weak. Consequently the mere existence of a lone pair of electrons on the base is not in itself sufficient to guarantee the formation of a stable adduct, and other factors such as base strength and steric considerations obviously play a role.

The most convenient way of preparing borane adducts is usually to react the base in excess with diborane(6), which, in cases where it is cleaved symmetrically, gives the required adduct in a facile reaction, e.g.[168]

$$2NMe_3 + B_2H_6 \rightarrow 2H_3B.NMe_3$$

But in the case of nitrogen the number of simple adducts that can be obtained as the sole product is restricted to those in which the nitrogen base is sufficiently bulky, e.g. $H_3B.N_2R_2$[169], $H_3B.NC_5H_5$[170] and $H_3B.NC_5H_4R$.[171] A different type of product, one arising from asymmetric cleavage of the B_2H_6 (p. 84), is formed when the base is small. This kind of limitation does not arise with bases containing other donor elements such as phosphorus or sulphur, for which asymmetric cleavage is not favoured (except in rare instances at elevated temperatures).

Other methods for preparing borane(3) adducts are available. In some cases displacement from the BF_3 adduct[172] or a mono-, di-, or tri-alkylborane adduct[173] will occur quantitatively:

$$2F_3B.PMe_3 + B_2H_6 \xrightarrow{80^\circ C} 2H_3B.PMe_3 + 2BF_3$$

It is a matter of relative stability. Disproportionation of mono- and di-alkylborane adducts to borane adducts has also been observed[174]:

$$3H_2MeB.NMe_3 \xrightarrow{200^\circ C} 2H_3B.NMe_3 + Me_3B.NMe_3$$

Alternatively the basic moiety may be changed by reaction, e.g.[175],

$$H_3B.PF_3 + 6NH_3 \xrightarrow[>25^\circ C]{Et_2O} H_3B.P(NH_2)_3 + 3NH_4F$$

or the acidic moiety, as when a trichloroborane adduct is reduced by heating with hydrogen under pressure[176]:

$$Cl_3B.NMe_3 + 3H_2 + 3NMe_3 \xrightarrow[2000\text{ atm}]{200^\circ C} H_3B.NMe_3 + 3NHMe_3Cl$$

Other modes of preparation commence with a tetrahydroborate[177–8]:

$$LiBH_4 + NH_4Cl \xrightarrow{Et_2O} H_3B.NH_3 + LiCl + H_2$$

$$NaBH_4 + PEt_2Cl \xrightarrow{\text{diglyme}} H_3B.PHEt_2 + NaCl$$

The latter procedure has been found useful in the preparation of trideuteroborane adducts:[179]

$$NaBD_4 + NHMe_3Cl \xrightarrow{C_4H_8O} D_3B.NMe_3 + NaCl + HD$$

Borane adducts are also formed with bidentate and polydentate donors, so that compounds such as $N_2H_4.2BH_3$[180–1] and $P_2Me_4.2BH_3$[182–3] are known as well as the corresponding mono adducts (however, with diborane(6), P_2F_4 gives no sign of a bis adduct, only $P_2F_4.BH_3$[184]). The phosphorus methylimide $P_4(NMe)_6$ forms adducts $P_4(NMe)_6(BH_3)_n$ containing 1, 2, 3 or 4 borane(3) groups, and with these compounds n.m.r. studies have indicated that the boron atoms are linked to the phosphorus atoms[185], as is also found in adducts such as $P_2(NMe_2)_4.2BH_3$.[186] Generally speaking, when a ligand contains two directly linked non-equivalent donor atoms, one of which is in the first and the other in the second short period, the BH_3 group prefers to link to the heavier donor first, while the tendency of the lighter donor to link up with a second BH_3 group may be so far reduced that a bis adduct is not formed. It is thus also in all probability true, that in adducts of formula $MeSNR_2.BH_3$ the boron atom is linked to the sulphur atom, since rearrangement to $MeSBH_2.NHR_2$ readily occurs, while on heating $MeSBHNR_2$ is formed with the loss of hydrogen.[187]

The stabilities of simple borane complexes vary over a wide range. If the base is strong, a relative stable solid complex with only a low dissociation pressure is likely to result. Thus at 25°C $H_3B.NMe_3$ has a vapour pressure of <1 Torr and possesses a B—N bond dissociation energy equal to $\frac{1}{2}D(H_3B\cdots BH_3)+18{\cdot}7$ kcal mol^{-1} (as calculated from thermochemical data[188–9]). But the corresponding adduct with the much weaker base dimethyl ether, $H_3B.OMe_2$, already exerts a pressure of 18 Torr at $-78{\cdot}5$°C and is completely dissociated in the vapour phase.[190] Also, with donors such as NMe_3, the acceptor power decreases in the order $BBr_3 > BCl_3 > BF_3 > \frac{1}{2}B_2H_6$[191], but it must be remembered that the true acceptor power of BH_3 is higher than the apparent acceptor power (as measured relative to diborane(6)) by an amount equal to one-half of the bridge-bond dissociation energy of diborane, and is thus almost certainly larger than for any of the boron trihalides.

At all events, not only is BH_3 a much stronger Lewis acid than BF_3 (in which the acceptor powers of the boron atom may be assumed to be considerably reduced by π bonding arising through back coordination from the fluorine atoms), but the order of adduct stability with phosphorus, sulphur or selenium compounds becomes $\frac{1}{2}B_2H_6 > BF_3$. The extreme instability of the borane(3) complexes with many ethers arises essentially from the circumstance that on dissociation the complex is in equilibrium not with borane(3) but with diborane(6), the energy recovered from the formation of the bridge bond being almost sufficient to dissociate the relatively rather weak coordinate bond of the complex: thus the existence of $H_3B.OEt_2$, for example, is barely demonstrable, and then only at low temperatures.

The compounds $H_3B.PMe_3$, $H_3B.AsMe_3$, $H_3B.SMe_2$ and $H_3B.SeMe_2$ are much more stable than $H_3B.OMe_2$. This has led to the observation[172,192] that, otherwise than with BF_3, with which the strength of coordination falls in the sequences $NMe_3 > PMe_3 > AsMe_3$ and $OMe_2 > SMe_2 > SeMe_2$, the orders for BH_3 are changed and must now be written $PMe_3 > NMe_3 > AsMe_3$ and $SMe_2 > SeMe_2 > OMe_2$ respectively. The explanation originally advanced, that hyperconjugation of the BH_3 group permits π bonding with vacant *d* orbitals of the donor atom in the case of atoms other than nitrogen and oxygen, is probably not the correct one. At least, hyperconjugation is relatively unimportant. (This conclusion finds a measure of support in recent theoretical work based on the hybrid orbital force field (HOFF) model.[193]) Rather, as must be emphasized, evidence from other systems containing B—H bonds indicates that the relative strength of a Lewis base with respect to a reference acid depends principally on the strength of the acid, so that as the acid becomes increasingly stronger, the σ bond formed between the donor and the boron atoms also increases in strength, eventually tending to reverse the sequence more usually observed[194] (see also the section on diborane(6), p. 118).

By means of force-constant calculations based on infra-red and Raman studies of borane(3) complexes with both neutral and charged ionic species, the foregoing sequences interrelating the strengths of the coordinate bonds with BH_3 have been extended as follows: $F^- > CN^- > NC^- > H^- > CO > PF_3 > PH_3$.[195] The bonding in borane(3) complexes has also been studied by photoelectron spectroscopy.[196]

The variation in the dissociation energy of the coordinate bond in borane(3) adducts is reflected in the physical properties (especially the volatility), and these are given for some of the simpler adducts in Table VI. The table is selective because the total number

Table VI.—Physical Properties of some Adducts of Borane(3)

Adduct	Melting point (°C)	Boiling point (°C)	Constants in equation $\log_{10} p_{\text{Torr}} = -A/T + B$		Enthalpy of vaporization$^{(a)}$ ΔH		Trouton constant		Ref.
			A	B	(kJ mol^{-1})	(kcal mol^{-1})	(J mol^{-1} K^{-1})	(cal mol^{-1} K^{-1})	
$H_3B.CO$ liquid	−137·0	−64	1040	7·85	19·91	4·76	96	22·8	168
$H_3B.NH_3$ solid	121–124$^{(b)}$	Vapour pressure 0·1 Torr at 80°C (sublimable$^{(b)}$)							197
$H_3B.NMe_3$ solid	95·55		2962	9·894	56·70$^{(c)}$	13·55$^{(c)}$			198, 189
$H_3B.NMe_3$ liquid		171	2202	7·846	42·16	10·08	95	22·7	168
$H_3B.NC_5H_5$ liquid	10–11	Vapour pressure 1·8 Torr at 99°C							170
$H_3B.NCMe$ solid			1640	7·285	31·40$^{(c)}$	7·50$^{(c)}$			199
$H_3B.PH_3$ solid	32–33$^{(d)}$	Vapour pressure 200 Torr at 0°C							200, 201
$H_3B.PMe_3$ solid	103–103·5		2933	9·531	56·15$^{(c)}$	13·42$^{(c)}$			202
$H_3B.P(SiMe_3)_3$	100–107	(Decomposes, evolving $SiHMe_3$, at 125°C)							203, 204
$H_3B.P(NMe_2)_3$	32·5	49–50							205
$H_3B.P(OMe)_3$ liquid		Vapour pressure 23 Torr at 86°C							206
$H_3B.PF_3$ liquid	−116·1	−61·8$^{(e)}$	1038·9	7·8061	19·89	4·75	94	22·5	207
$H_3B.AsMe_3$ solid	73·5–74·5		2920	9·966	55·90$^{(c)}$	13·36$^{(c)}$			208
$H_3B.AsMe_3$ liquid		154$^{(e)}$	2420	8·553	46·33	11·07	108	25·9	166, 208
$H_3B.SbMe_3$	−35$^{(f)}$	(Decomposes or completely dissociates above −35°C)							209
$H_3B.OMe_2$	≫ −78·5	Vapour pressure 18 Torr at −78·5°C and > 760 Torr at the m.p.							190, 210
$H_3B.OC_4H_8$ liquid	−45	62$^{(e)}$	1244	6·592	23·82	5·69	71	17·0	211
$H_3B.SMe_2$ liquid	−40 – −38	97$^{(e)}$	2346	9·220	44·91	10·73	121	29·0	212
$H_3B.SC_4H_8$ liquid	−30 – −35	132·5$^{(e)}$	2321	8·602	44·43	10·62	110	26·2	211
$H_3B.S(NMe_2)_2$	64–65	(Decomposes, evolving H_2, > 65°C)							213
$H_3B.SeMe_2$ liquid	−34 – −32	63·2$^{(e)}$	1732	8·030	33·16	7·92	99	23·5	192

(a) Calculated from the vapour-pressure equation.
(b) With some decomposition
(c) Refers to sublimation.
(d) Under increased pressure.
(e) Extrapolated.
(f) Decomposition temperature rather than a true melting point.

of adducts known is now too large for any attempt at comprehensiveness; a further table of less simple adducts studied between 1964 and 1969 has been published[214] and occupies 9 pages. The n.m.r. spectra of many of the adducts have been recorded, and the ^{11}B chemical shifts listed along with those of other types of boron compounds in a useful book.[215]

Also of interest is the way in which the BH_3 group reorganizes itself upon coordination, depending on the nature of the donor. The manner in which the frequencies of the B—H valency vibrations shift has been investigated for certain complexes with substituted phosphines and amines.[216] Constitutive changes in the ^{11}B and ^{13}C n.m.r. spectra have also been studied[217–18], as have changes in magnetic rotatory power and molecular refraction.[219–22] One theoretical study has led to the conclusion that for the reorganization of the BH_3 group the σ bond interaction with the donor exerts a much greater influence than any π bond interaction.[193]

The chromatographic behaviour of many borane(3) adducts has been investigated.[223–4]

On heating, many BH_3 complexes undergo changes other than reversible dissociation.[190] There are two principal ways in which this may occur. One is polymerization, usually accompanied by the shifting of hydrogen from the boron atom to another atom: thus, for example, above 20°C the adduct of methyl cyanide, $MeCN.BH_3$, trimerizes to 1,3,5-triethylborazine $(MeCH_2NBH)_3$.[199] The other is to split off hydrogen or some other simple hydrogen-containing molecule irreversibly, which presupposes that the donor atom has a hydrogen atom or some suitable group such as SiH_3 attached to it. Burg has discussed some cases for which the rates of hydrogen evolution have been observed to differ widely.[190]

The hydridic nature of the B—H bonds is considerably modified on coordination of the boron atom, as is clear from other reactions of BH_3 adducts. Thus, although BH_3 doubtlessly undergoes immediate hydrolysis on contact with water as does its more stable dimer B_2H_6, the adduct $Me_3N.BH_3$ is so slowly hydrolyzed, that it is possible to deuterate it by exchange over several hours with acidified D_2O.[225] And unlike the monohalogenated diboranes such as B_2H_5Cl (which are very labile and disproportionate moderately rapidly at room temperature) the monohalogen derivatives of amine boranes, e.g. $Me_3N.BH_2Cl$ and $Me_3N.BH_2Br$, are preparable from the amine borane by a mild halogen-exchange reaction with the appropriate N-halogenosuccinimide and are stable solids with definite melting points.[226] Monochloroborane complexes of phosphines are prepared similarly from the phosphine boranes.[227] With $H_3P.BH_3$, halogen substitution at the boron atom is also readily effected by HCl or HBr.[228]

Infra-red studies have shown that many BH_3 adducts in an inert solvent (CCl_4) form hydrogen bonds of the type $OH\cdots BH_3$ with hydroxyl compounds such as methanol and phenol.[229]

ADDUCTS WITH METAL COMPOUNDS

Alkali metal hydrides such as LiH or NaH will add on BH_3, but do so readily only in the presence of a solvent capable of dissolving the product, which is a metal tetrahydroborate.[230–2] A suitable solvent is a polyether, and further addition of BH_3 in solution to form a heptahydrodiborate[233] may occur. The last step finds a parallel in the reactions of salts of certain hydropolyborates, which likewise add on BH_3.[234]

$$NaH \xrightarrow[\text{diglyme}]{(BH_3)} NaBH_4 \xrightarrow[\text{diglyme}]{(BH_3)} NaB_2H_7$$

$$KB_4H_9 \xrightarrow[Me_2O]{(BH_3)} KB_5H_{12}$$

$$KB_5H_8 \xrightarrow[Et_2O]{(BH_3)} KB_6H_{11}$$

$$n\text{-}Bu_4NB_6H_9 \xrightarrow[CH_2Cl_2]{(BH_3)} n\text{-}Bu_4NB_7H_{12}$$

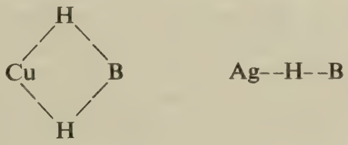
So far, however, the reactions have only been studied in solution.

In the presence of an ether, other hydrides will add on BH_3. Thus BeH_2 forms BeB_2H_8 (but heating is necessary)[235], while MgH_2 and CaH_2 give $Mg(BH_4)_2$[236–7] and $Ca(BH_4)_2$[238] respectively. Likewise AlH_3 yields $Al(BH_4)_3$ via the identifiable intermediates AlH_2BH_4 and $AlH(BH_4)_2$.[239] Alkoxyaluminium hydrides $[(RO)_nAlH_{3-n}]_x$ are similarly convertible to the corresponding alkoxyaluminium tetrahydroborates.[240] The tetrahydroaluminate anion AlH_4^- will add on BH_3 to give an anion of the formula $AlBH_7^-$, which rearranges to the more stable $[AlH_3(BH_4)]^-$ anion.[241] The latter in turn will take up more BH_3 to give successively the $[AlH_2(BH_4)_2]^-$, $[AlH(BH_4)_3]^-$ and even the $[Al(BH_4)_4]^-$ anions[242–5], though the formation of some of the intermediate complex ions has been disputed.[246] In a similar manner the complex $Me_3N.AlH_3$ is converted to $Me_3N.Al(BH_4)_3$.[247] The GaH_4^- anion is likewise converted to anions of the general formula $[GaH_{4-n}(BH_4)_n]^-$ ($n = 1, 2, 3, 4$).[242] In most of these compounds the boron is probably linked to the metal via a pair of bridging hydrogen atoms.

The behaviour of organometallic compounds is not everywhere straightforward. Although it has been claimed that phenyllithium LiPh takes up BH_3 to form the trihydrophenylborate $LiBH_3Ph$[248], other workers have found different initial products arising from substitution rather than addition.[249] Lithium alkyls such as LiMe and LiEt certainly appear to react differently[249–50], while the reactions of alkyls of the other alkali metals have not been studied in this respect. No addition compounds have so far been identified from dimethylberyllium $BeMe_2$, but some of the products remain unidentified.[251–2] It is not unlikely that addition initially occurs, since diethylmagnesium $MgEt_2$ gives $EtMgBH_3Et$ and $Mg(BH_3Et)_2$[253–5], among other products. In as far as other metal alkyls have been examined, no addition products have been observed.

Certain metal carbonyl anions give borane(3) adducts, of which the ions $[H_3BMn(CO)_5]^-$, $[H_3BMn(CO)_4PPh_3]^-$, $[H_3BRe(CO)_5]^-$ and $[(H_3B)_2Re(CO)_5]^-$ have been identified[256], while the metal nitrosyl, trinitrosylcobalt $Co(NO)_3$, is apparently converted by diborane(6) to the BH_3 adduct $(ON)_3Co.BH_3$.[257]

Complexes of copper(I) and silver(I), notably $(Ph_3P)_3CuCl$ and $(PhP)_3AgNO_3$, react with the O-ethylboranocarbonate $KH_3BCOOEt$ to give compounds of respective formulae $(Ph_3P)_2CuH_3BCOOEt$ and $(Ph_3P)_3AgH_3BCOOEt$.[258] The observed infra-red frequencies suggest that the BH_3 groups are linked to the metal through two and one bridging hydrogen atoms respectively:



BORANE CARBONYL

Relatively few BH_3 adducts in which the boron is directly linked to a Group-IV element are known, but particular interest is centred on borane carbonyl $H_3B.CO$, first reported in 1937 and since then the object of much study. The original preparation was from diborane(6) and excess carbon monoxide under pressure at 90°–100°C[168]:

$$B_2H_6 + 2CO \rightleftharpoons 2H_3B.CO$$

At room temperature equilibration is too slow for convenience. The product is readily isolable but must be stored at low temperatures to avoid progressive decomposition. An alternative preparation which dispenses with the need for heat and pressure is to carry out the reaction in monoglyme at −45°C or in diethyl ether at −60°C.[214] (Other ether solvents such as tetrahydrofuran and dimethyl ether compete for the BH_3 and form ether.BH_3 complexes.) Preparation of $H_3B.CO$ from carbon monoxide and boroxine has also been realized.[259]

Molecular parameters of $H_3B.CO$ have been established from microwave[167], infrared[260–1], Raman[262] and photoelectron[196] spectra. In addition, high-resolution infrared studies of the B—C ν_2 and ν_4 stretching-vibration bands and of certain parallel and

Table VII.—Miscellaneous Molecular Properties of Borane(3) Carbonyl

Parameter	Species	Value
Interatomic distance (Å)[a]	B—H	1·194
	B—C	1·540
	C—O	1·131
Interbond angle[a]	H—B—H	113° 52′
	H—B—C	104° 36′[b]
Principal moment of inertia (g cm² × 10⁻⁴⁰)[a]	$^{11}BH_3.CO$	96·90
	$^{10}BH_3.CO$	93·43
	$^{11}BD_3.CO$	114·35
	$^{10}BD_3.CO$	111·41
Stretching force constant (mdyne Å⁻¹)[c]	B—H	3·30
	B—C	2·79
	C—O	17·94
Ionization potential (eV)[d]	$BH_3.CO$	11·14
Dipole moment (D)[e]	$BH_3.CO$	1·795

[a] Ref. 167.
[b] Calculated in Ref. 195 from the data in Ref. 167.
[c] Ref. 195.
[d] Ref. 196.
[e] Ref. 267.

perpendicular bands have been reported for isotopic species of $H_3B.CO$.[263–6] The principal results are given in Table VII.

Since carbon monoxide is usually reckoned as a weak donor, it is of some surprise to find that the B←C bond length is 1·540 Å, virtually identical with the C—C distance in ethane and shorter than the B—C distance (1·56 Å) in trimethylborane.[268] The reason for this short distance is not known, although hyperconjugation associated with π bonding has frequently been suggested. It is, however to be expected that with the change in configuration of the BH_3 molecule on coordination the formerly vacant p orbital assumes an appreciable degree of s character. One theoretical treatment indicates that the s character amounts to c. 16% with respect to the boron atom.[193] The results of various theoretical studies—based respectively on a standardized set of symmetry coordinates[269–70], the CNDO[271–2] and INDO approximations[271–3], a Green's function analysis[274], the HOFF-model treatment[193–5], virial partitioning[145] and *ab initio* SCF[275], CI[275] and MO[276] treatments—have been compared with experiment. No compelling conclusions in favour of hyperconjugation have been drawn.

Borane carbonyl has a somewhat versatile chemistry. The carbon monoxide is completely displaced by trimethylamine (although there is evidence for the existence of an adduct $H_3BC(O)NMe_3$, isolable at low temperatures), but not by dimethylamine, methylamine or ammonia, which react differently[277] (see below). With NMe_3 the reaction is exothermic, but proceeds with an activation energy of $8{\cdot}60 \pm 0{\cdot}30$ kcal mol⁻¹.[278] Methylphosphine PH_2Me behaves similarly.[279] Below −130°C NO will likewise replace CO to give traces of the exceedingly unstable complex $H_3B.NO$[280], though the principal products are N_2O and boric acid H_3BO_3. Borane carbonyl does not react with N_2O.[281] Hydrolysis is rapid and less simple than once supposed, involving a temperature-dependent competition between two reactions[282]:

$$H_3BCO + 3H_2O \rightarrow B(OH)_3 + 3H_2 + CO$$

$$H_3BCO + 2H_2O \rightarrow (HO)_2BCH_2OH + H_2$$

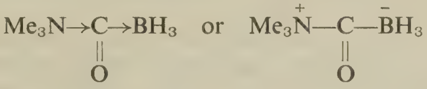
The proportion of dihydroxy(hydroxymethyl)borane, which arises through reduction of the carbonyl group, increases as the temperature is reduced. The reaction of H_3BCO with oxygen under controlled conditions has received study.[283]

It has been noted that the BH_3 group is isoelectronic with the oxygen atom, so that H_3BCO may be compared with CO_2. On this view it should give rise to salts of the boranocarbonate ion $H_3BCO_2{}^{2-}$ and the boranobicarbonate ion H_2BCOOH^- and even to boranocarbonic acid $H_3BC(OH)_2$, analogous to the carbonates and carbonic acid, as is in fact observed[284, 282], e.g.:

$$\mathrm{CaO + H_3BCO \xrightarrow{H_2O\ (trace)} Ca[H_3BCO_2]}$$
$$\mathrm{NaOH + H_3BCO \longrightarrow Na[H_3BCOOH]}$$

Similarly the compound formed with ammonia, $H_3BCO.2NH_3$[168], might be likened to a carbamate, and the boranocarbamate structure $NH_4{}^+[H_3BCONH_2]^-$ has indeed received support from chemical, infra-red and X-ray diffraction studies, as have the structures of analogous compounds, salts of the N-methylboranocarbamate and N,N-dimethylboranocarbamate anions, that are formed with mono- and di-methylamines respectively.[277, 285] However, the electronic similarity between $H_3B.CO$ and CO_2 must not be overemphasized, since with potassium glycinate $K[H_2NCH_2COO]$ the latter effects carbamate formation, while the former merely gives the 1 : 1 adduct potassium N-boranocarboxylatoaminoacetate, $K[H_3BC(O)NH_2CH_2OO]$[286]—although an alternative structure involving the migration of a hydrogen atom from nitrogen to oxygen is not excluded.

Tertiary amines cannot react in a precisely analogous way to ammonia and primary and secondary amines (see above), but form simple 1:1 adducts reversibly at low temperatures, e.g. $H_3BC(O).NMe_3$, which by infra-red and ^{11}B n.m.r. spectroscopy has been shown to have the following structure[287–8]:

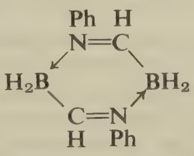


$$\mathrm{Me_3N{\rightarrow}\underset{\overset{\|}{O}}{C}{\rightarrow}BH_3 \quad or \quad Me_3\overset{+}{N}—\underset{\overset{\|}{O}}{C}—\overset{-}{B}H_3}$$

Pyridine does not form an analogous compound, but triphenylphosphine gives $H_3BC(O).PPh_3$.[287]

OTHER ADDUCTS WITH COMPOUNDS OF GROUP-IV ELEMENTS

Borane(3) forms adducts with a few other compounds of carbon. It might be expected that covalent isocyanides RN—C, in which the electronic state of the carbon is similar to that in carbon monoxide, should likewise give BH_3 adducts. But with phenyl isocyanide PhNC, at least, the simple adduct (which is not isolated) apparently undergoes a hydrogen shift and immediately dimerises[289] to the cyclic compound



The cyanide ion CN^-, which is isoelectronic with CO, differs from it in forming both a monoadduct $[H_3B.CN]^-$ [290] and a bis adduct $[H_3B.CN.BH_3]^-$.[291] In addition to their alkali metal salts, tetrasubstituted ammonium salts are readily prepared.[292] The ion $[H_3B.CN]^-$ is more stable than its isomer $[H_3B.NC]^-$ [293] and has selective reducing properties.[294–5] Surprisingly it undergoes hydrogen exchange with the hydrogen of nitrogen bases.[296] Both $[H_3B.CN]^-$ and $[H_3B.NC]^-$ have been subjected to theoretical treatment.[193, 195, 270] The boron is apparently linked to carbon in the bis adduct with the 1,10-phenanthroline isocyano complex of iron, $Fe(phen)_2(NC.BH_3)_2$[297], as may also be true in the complex cyanate anion $[H_3B.CNO]^-$ [298], but this is uncertain.

Another group of adducts in which the BH_3 group is directly linked to carbon is formed by the ylides such as methylenetriphenylphosphorane $Ph_3\overset{+}{P}—\overset{-}{C}H_2$, which gives a complex that may be written $Ph_3P \rightarrow CH_2 \rightarrow BH_3$ or $Ph_3\overset{+}{P}—CH_2—\overset{-}{B}H_3$.[299–300] Ylides containing arsenic instead of phosphorus react in a comparable manner[301], as do those containing sulphur[302], but in the latter case rearrangement occurs with the elimination of an organic sulphide (p. 131).

The only known borane(3) adducts in which the boron is directly linked to silicon or germanium are those of the silyl and germyl anions SiH_3^- and GeH_3^-, which are converted by diborane(6) into the ions $[H_3B.SiH_3]^-$ [303] and $[H_3B.GeH_3]^-$ [304] respectively. The products are exceedingly unstable and break up spontaneously into other compounds.

ADDUCTS WITH COMPOUNDS OF NITROGEN

Ammonia Borane

A large number of borane(3) adducts is known in which a nitrogen atom constitutes the donor, the simplest being ammonia borane $H_3N.BH_3$. But the compound ordinarily formed from the interaction of ammonia and diborane(6) is mainly or entirely an ionic one with the same stoichiometry, namely $[H_2B(NH_3)_2][BH_4]$. This can, however, be converted into $H_3N.BH_3$ by treating it while suspended in ether with ammonium chloride[177, 305] or a lithium salt[306]:

$$[H_2B(NH_3)_2][BH_4] + NH_4Cl \xrightarrow[\text{trace } NH_3]{Et_2O} [H_2B(NH_3)_2]Cl + H_3B.NH_3 + H_2$$

$$[H_2B(NH_3)_2][BH_4] \xrightarrow[Et_2O]{LiX} \frac{1}{n}(H_2NBH_2)_n + H_2 + H_3B.NH_3$$

The effect of the lithium salt is essentially catalytic and has been interpreted in terms of the high polarizing power of the Li^+ cation. Alternatively the conversion to $H_3B.NH_3$ is effected essentially without loss if it is allowed to stand for a few days at room temperature in diglyme containing a little B_2H_6.[307] But by modifying the original procedure and introducing the NH_3 to the B_2H_6 dissolved in tetrahydrofuran at low temperatures, it is possible to make $H_3B.NH_3$ directly[308]: the yield is about 50%, and after evaporation of the solvent the adduct is separated from the accompanying ionic isomer $[H_2B(NH_3)_2][BH_4]$ by extraction with ether. In another modification the two gases are passed simultaneously at room temperature into ether, dioxan, or even water[309] (for $H_3B.NH_3$ is hydrolytically stable towards cold water). Other methods of preparation involve the action of $LiBH_4$ on NH_4Cl[177] (p. 11) or the interaction of NH_3 with $NaBH_4$ plus I_2[310], or alternatively with $H_3B.OC_4H_8$[308], $H_3B.OMe_2$[305] or $H_3B.SMe_2$[197]

$$H_3B.SMe_2 + NH_3 \xrightarrow{-20°C} H_3B.NH_3 + SMe_2$$

In all of these procedures the ionic isomer is a by-product.

Unlike the latter, $H_3B.NH_3$ is sublimable in a vacuum.[305] In addition it is soluble in ether or dioxan, in both of which it is monomeric[308], as it is in liquid ammonia.[305]

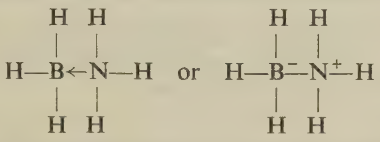
The structure is known[311–12] and bears a close relationship to that of ethane. Infra-red spectra and vibrational assignments for $H_3B.NH_3$, $H_3B.ND_3$ and $D_3B.ND_3$ were obtained from work on samples isolated in an argon matrix at 20 K.[313] This has led, rather unexpectedly, to a reassignment of the stretching frequencies for the $^{11}B—N$ bond to 968, 945 and 912 cm^{-1} respectively, which corresponds to a stretching force constant of 4·56 mdyne $Å^{-1}$, values very much higher than those accepted earlier.[314] The coordinate bond is therefore now to be regarded as decidedly strong and fairly closely comparable in strength with the C—C covalent bond in the isoelectronic molecule C_2H_6, for which the stretching frequency is 994·8 cm^{-1} [315] and the force constant 4·45 mdyne $Å^{-1}$.[316] The B—N bond length, $1{\cdot}56 \pm 0{\cdot}05$ Å[311], is also similar to the C—C bond length, 1·54 Å. There are, however marked differences in the physical properties of the two compounds apart from the very obvious difference in the volatility (C_2H_6 is a gas, b.p. −88·6°C, $H_3B.NH_3$ is a slightly volatile solid, v.p. 0·1 Torr at 80°C, m.p. 121°–124°C).[197] The ionization potential of $H_3B.NH_3$ is 9·44 eV derived

Table VIII.—Some Physical Properties of Ammonia Borane and the Mono-, Di- and Trimethylamine Boranes

Species	Melting point (°C)	Heat of sublimation[a] (kcal mol^{-1})	Ionization potential[b] (eV)	Dipole moment (D)
$H_3B.NH_3$	121–124[c]		9·44	5·01[d]
$H_3B.NH_2Me$	56[e]	18·8±1·0	9·66	5·02[d]
$H_3B.NHMe_2$	37[e]	18·5±0·7	9·39	4·93[d]
$H_3B.NMe_3$	95·5[f]	13·6±0·2	9·28	4·69[d] 4·59[g] 4·84[h]

(a) Ref. 189.
(b) Ref. 196.
(c) Ref. 197.
(d) Ref. 318.
(e) Ref. 319.
(f) Ref. 198.
(g) Ref. 320.
(h) Ref. 321.

from the photoelectron spectrum[196], more than 2 eV lower than that of C_2H_6 (11·63 eV[317]). Moreover $H_3B.NH_3$, in common with amine boranes (Table VIII), has a high dipole moment (5·01 D[318]). Although a theoretical approach has predicted the molecular strength with considerable accuracy[322], the question of the charge transfer associated with the B—N bonding cannot be said to be unequivocally settled. The matter is unquestionably one of great interest and theoretical importance. The photoelectron spectrum appears to indicate σ bonding[196]—and this is borne out by theoretical treatment based on *ab initio* molecular-orbital calculations[323], Gaussian-type atomic orbitals[324] and the HOFF model[193], respectively—but the electron distribution is nevertheless probably very poorly depicted by the usual representation in which the boron and nitrogen atoms have respective formal charges of −1 and +1:



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & B & \leftarrow & N & -H \\ & | & & | & \\ & H & & H & \end{array} \quad \text{or} \quad \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & \overset{-}{B} & - & \overset{+}{N} & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Rather, another theoretical study based on a non-empirical SCF–LCAO method using Gaussian orbitals has predicted a negative charge (−0·822) for the N atom and an almost zero charge for the B atom.[325] The picture obtained from an extended Hückel LCAO–MO method[326–7] is qualitatively similar. But a Hartree–Fock approach based on Gaussian functions has led to a picture in which the charge transfer is equivalent to a transfer of about 0·25 electron from the nitrogen to the boron[328], and the figure resulting from a CNDO/2D treatment is not very different, namely 0·33 electron.[329] The direction of the electric dipole is of course linked up with this question, but the other bonds in the molecule are believed to make an appreciable contribution to the high moment referred to. *Ab initio* LCAO–MO–SCF studies of this molecule have also been undertaken.[330–2]

The chemistry of ammonia borane has been inadequately studied, partly, no doubt, because of the difficulty of obtaining it pure. The original claim[305] that it is slowly converted to the dimer $[H_2B(NH_3)_2][BH_4]$ has been disproved.[307] Likewise the statement that it slowly evolves H_2 at room temperature[305] must be attributed to the presence of impurities, since the sublimed material is stable for several days at 70°C.[197] It can be sublimed with slight decomposition at 80°C, the first decomposition product being boranamine (aminoborane) H_2BNH_2[333], which immediately polymerizes.

$$H_3B.NH_3 \xrightarrow[-H_2]{\text{heat}} [H_2BNH_2] \rightarrow \frac{1}{n}(H_2BNH_2)_n$$

At progressively higher temperatures, especially above the melting point, loss of hydrogen is more rapid, and further decomposition to borazine $B_3N_3H_6$, borimide $B_2(NH)_3$, and even boron nitride BN may occur.[334]

Amine Boranes

Amines form similar compounds with borane(3), the amine boranes, and many of these have been much better characterized. They have been reviewed.[335] Unlike trimethylamine NMe_3, the primary and secondary amines NH_2Me and $NHMe_2$ cleave diborane(6) asymmetrically, mainly or in part[336–7], so that $H_3B.NH_2Me$ and $H_3B.NHMe_2$ are best prepared in ways comparable to those mentioned for $H_3B.NH_3$. The complex $H_3B.NH_2Et$ has been prepared by the electrolysis of $NaBH_4$ in ethylamine[338] and this method doubtless has wider applications. But the asymmetric cleavage products slowly rearrange to the monomeric adducts; so at least the salt obtained from methylamine[337]

$$[H_2B(NH_2Me)_2][BH_4] \xrightarrow[\text{several months}]{\text{room temperature}} 2H_3B.NH_2Me$$

Generally speaking, the amine boranes are crystalline solids of some volatility with definite melting points, and are monomeric in solution. Table VIII gives the melting points[319,168,189], heats of sublimation[189], ionization potentials[196] and dipole moments[318] of $H_3B.NH_2Me$, $H_3B.NHMe_2$ and $H_3B.NMe_3$, which compounds have been well characterized. The vapour pressure increases and the heat of sublimation decreases with progressive substitution of H by CH_3. Some infra-red[339], Raman[340], n.m.r.[341] and photoelectron spectra[196] have also been reported, as has a theoretical study.[329] There is evidence that the coordinated BH_3 group of such compounds can participate (as a proton acceptor) in hydrogen bonding with hydroxy compounds. At least, in the case of $H_3B.NHMe_2$[336] this appears to occur with methanol or phenol.[342]

Thermally, the borane(3) adducts of the methylamines are stable up to their melting points and a little above, but at higher temperatures $H_3B.NH_2Me$ and $H_3B.NHMe_2$ lose hydrogen, in the case of the former to form trimeric N-methylboranamine (1,3,5-trimethylcyclotriborazane) and ultimately 1,3,5-trimethylborazine[343–4]:

$$3H_3B.NH_2Me \xrightarrow[-3H_2]{100°C} (H_2BNHMe)_3 \xrightarrow[-3H_2]{190°C} (HBNMe)_3$$

(The first stage occurs via identifiable intermediates.[343]) Amine boranes are reactive **and readily halogenated at the boron; e.g. the reaction of $H_3B.NH_2(t\text{-Bu})$ with HX [X = Cl, F] to give $X_3B.NH_2(t\text{-Bu})$ has been studied.[345]**

A useful preparation of $H_3B.NHMe_2$ is to treat the amine with $NaBH_4$ and I_2.[346] With $H_3B.NHMe_2$, hydrogen elimination occurs at about 190°C and necessarily stops after the first stage[347]; from the behaviour of $H_3B.NDMe_2$ and $D_3B.NHMe_2$ it has been shown to take place by a bimolecular reaction.[348] The compound has been observed to possess a certain acidity at its amino hydrogen atom and will react with alkali metals and their hydrides to form salts of the dimethylamidotrihydroborate ion $[Me_2NBH_3]^-$[291,349]:

$$2H_3B.NHMe_2 + 2Na \xrightarrow[-40°C]{\text{liq. } NH_3} 2Na[Me_2NBH_3] + H_2$$

$$H_3B.NHMe_2 + NaH \xrightarrow[45°C]{\text{glyme}} Na[Me_2NBH_3] + H_2$$

Hydrogen is also eliminated on reaction with phenol[350]

$$H_3B.NHR_2 + PhOH \xrightarrow{\text{heat}} HB(OPh)NR_2 + 2H_2$$

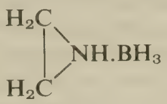
Dimethylchloramine is reduced[351]

$$H_3B.NHMe_2 + Me_2NCl \rightarrow [BH_2(NHMe)_2]Cl$$

Because of its useful reducing powers, $H_3B.NHMe_2$ has been used in the reduction of an alicyclic ketone[352]; together with other amine boranes it has additional uses as a reducing agent, both in electroplating[353] and electroless plating processes.[354–7]

Ethylenediamine, a bidentate primary amine, forms the bis-borane adduct

$H_3B.NH_2CH_2CH_2NH_2.BH_3$, which has been shown to have an open-chain molecular structure with a *trans* configuration.[358] An interesting adduct of a cyclic secondary amine, aziridine borane



has recently been described and studied[359–61], and also treated theoretically.[362] The adduct of the related imine, ketimine $Ph_2C{=}NH$, is unusual in losing hydrogen to give a borazine directly and not the expected substituted borane $Ph_2C{=}NBH_2$[363]

$$\underset{\text{diphenylketimine borane}}{3Ph_2C{:}NH.BH_3} \xrightarrow[-3H_2]{120°C} \underset{\text{1,3,5-tris(diphenylmethyl)borazine}}{(HBNCHPh_2)_3}$$

It may be suspected that $Ph_2C{=}NBH_2$ is formed as an intermediate, but rapidly undergoes rearrangement with a hydrogen shift leading to trimerization.

Adducts with tertiary amines, like $H_3B.NMe_3$ and $H_3B.NEt_3$, have been particularly well studied. Unlike the former, $H_3B.NEt_3$ is a liquid at room temperature. These compounds are very conveniently prepared from the amine and B_2H_6 direct, as asymmetric cleavage of the latter does not occur here. However, it is not necessary to isolate the B_2H_6, which may be prepared *in situ* from $NaBH_4$ plus I_2.[310] Alternatively $H_3B.NMe_3$ can be formed from $[NHMe_3]Cl$ plus $NaBH_4$.[364]

The volatility of solid $H_3B.NMe_3$ exceeds that of the less completely methylated analogues discussed above, suggesting a progressive decrease in intermolecular hydrogen bonding in the solid phase with progressive methylation. The vapour pressure at 25°C is already 0·911 Torr.[189] The compound melts at 95·55°C[198] and boils at 171°C.[168] Table VI reproduces vapour-pressure equations for the solid and liquid phases, as well as the enthalpies of sublimation and vaporization. The enthalpy of fusion is $1182{\cdot}4 \pm 0{\cdot}8$ cal mol^{-1}, while that for $H_3B.NEt_3$ is $3562{\cdot}7 \pm 0{\cdot}9$ cal mol^{-1} at its melting point of $-3{\cdot}67$°C.[198]

The molecular parameters of $H_3B.NMe_3$ have been determined by microwave studies[320–1] and are reproduced in Table IX. The compound and (in part) its isotopic species have also been studied by infra-red[339, 365], Raman[340, 365], ultraviolet[366], mass-spectral[367] and n.m.r.[368] techniques. The last-mentioned has provided information

Table IX.—Some Molecular Properties of Trimethylamine Borane

Parameter	Species	Value
Interatomic distance (Å)	B—H	$1{\cdot}211 \pm 0{\cdot}003^{(a)}$
	B—N	$1{\cdot}638 \pm 0{\cdot}010^{(b)}$
	N—C	$1{\cdot}483 \pm 0{\cdot}01^{(b)}$
	C—H	$1{\cdot}111^{(a)}$
Interbond angle	H—B—N	$105{\cdot}32 \pm 0{\cdot}16°^{(a)}$
	B—N—C	$109{\cdot}9 \pm 1°^{(b)}$
	N—C—H	$106{\cdot}6°^{(a)}$
Stretching force constant (mdyn Å^{-1})	B—N	$2{\cdot}59 \pm 0{\cdot}09^{(c)}$
	N—C	$4{\cdot}91 \pm 0{\cdot}10^{(c)}$
	B—H	$2{\cdot}94 \pm 0{\cdot}02^{(c)}$
	C—H	$4{\cdot}90 + 0{\cdot}02^{(c)}$
Barrier to internal rotation of BH_3 (kcal mol^{-1})	$H_3B.NMe_3$	$3{\cdot}4^{(a)}$

(a) Ref. 320.
(b) Ref. 321.
(c) Ref. 365.

about molecular motions in the crystalline state.[369] Solution work with the aromatic solvents C_6D_6 and C_6F_6 has resulted in the observation of respective chemical shifts that lie in opposite directions.[370] In solutions of C_6H_6 and dioxane, other solute-solvent interactions of a stereospecific nature have been studied, and the polarization refraction, dipole moment, molar Kerr constant and polarizability determined and compared with the corresponding adducts of the boron trihalides.[368] It has also been shown that no exchange of free NMe_3 with $H_3B.NMe_3$ occurs in C_6H_6 on the n.m.r. time scale at temperatures up to 74°C.[371] The low potential barrier to rotation about the B—N bond[320] and various theoretical considerations[193, 365, 372] suggest that there is little π-bond interaction.

Reactions of amine boranes which have received study are isotope exchange and substitution at the boron atom, and hydride-ion abstraction. Catalyzed exchange with D_2 in toluene solution is complete in 24 h at 100°C.[373] Substitution reactions are of two kinds. In the first, the amine is substituted by another ligand, but the only donor strong enough to replace nitrogen is phosphorus: thus trimethylphosphine will displace trimethylamine.[192, 374]

$$H_3B.NMe_3+PMe_3 \rightarrow H_3B.PMe_3+NMe_3$$

It has been shown for a similar substitution using tributylphosphine that the displacement mechanism is S_N2–B.[375] A like mechanism is usually observed in displacement reactions with adducts of substituted borane(3), but examples of S_N1–B mechanisms and a mixture of the two types are known.[376–7]

The second kind of substitution reaction involves stepwise replacement of the hydrogen attached to the boron. Such reactions are a consequence of the reducing powers of the borane(3) moiety of the adduct, and in some cases stop with the substitution of one hydrogen atom. With complete substitution of all hydrogen atoms the reducing powers disappear. Examples are the reduction of organic chlorides[378]:

$$CPh_3Cl+H_3B.NR_3 \rightarrow H_2ClB.NR_3+CHPh_3$$

$$CCl_4+H_3B.NR_3 \rightarrow H_2ClB.NR_3+CHCl_3$$

The former reaction proceeds by a polar mechanism involving the forms $Ph_3C^+Cl^-$ and $R_3N.BH_2{}^+Cl^-$, and the latter by a free-radical mechanism:

$$CCl_4 \rightarrow CCl_3\cdot+Cl\cdot$$

$$CCl_3\cdot+R_3N.BH_3 \rightarrow R_3N.BH_2\cdot+CHCl_3$$

$$R_3N.BH_2\cdot+CCl_4 \rightarrow R_3N.BH_2Cl+CCl_3\cdot$$

Substitution also occurs with dimethylchloramine[351]

$$Me_2NCl+H_3B.NMe_3 \rightarrow H_2ClB.NMe_3+NHMe_2$$

Stepwise substitution is observed with elementary bromine:[345]

$$H_3B.NMe_3 \xrightarrow{Br_2} H_2BrB.NMe_3 \xrightarrow{Br_2} HBr_2B.NMe_3 \xrightarrow{Br_2} Br_3B.NMe_3$$

Fluorine is likewise completely substituted for hydrogen in stages by means of anhydrous hydrogen fluoride[379]

$$HF+H_3B.NMe_3 \xrightarrow[C_6H_6]{0°C} H_2FB.NMe_3+H_2, \text{ etc.}$$

Here, however, the affinity of boron for fluorine is so high, that reaction does not stop with the formation of $Me_3N.BF_3$, but will proceed further to give $[NHMe_3][BF_4]$. Salts of heavy metals likewise effect substitution[380]:

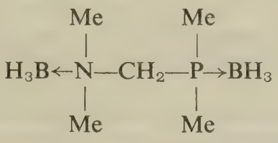
$$H_3B.NMe_3+2HgX_2 \rightarrow H_2XB.NMe_3+Hg_2X_2+HX \; [X = Cl, Br]$$

$$H_3B.NMe_3+AgCN \rightarrow H_2B(CN).NMe_3+Ag+\tfrac{1}{2}H_2$$

In reactions involving the abstraction of a hydride ion, amine boranes of type $H_3B.NR_3$ give $[H_2B(NR_3)_2]^+$ salts. Such reactions occur with iodine and amines[381] and with Ph_3CBF_4 in donor solvents.[382]

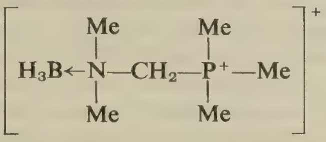
Though the reducing powers of the BH_3 moiety are considerably reduced on coordination to nitrogen, the complexes so formed are nevertheless useful, if comparatively mild, reducing agents. For example, $H_3B.NMe_3$ has been recommended for the convenient and rapid reduction of indoles to indolines.[383]

Because they are derivatives of NMe_3, the bases $Me_2NCH_2PMe_2$ and Me_2NCH_2SMe should be mentioned at this point. The latter forms a monoadduct with BH_3 in which the boron is linked to the nitrogen.[384] Although in the monoadduct of $Me_2NCH_2PMe_2$ the boron is linked to the phosphorus, additional bonding to the nitrogen occurs in the bis adduct[384]



$$H_3B\leftarrow\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{N}}-CH_2-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{P}}\rightarrow BH_3$$

But if the original base is methylated to give the ion $[Me_2NCH_2PMe_3]^+$, reaction with B_2H_6 results in the adduct cation



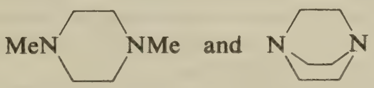
$$\left[H_3B\leftarrow\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{N}}-CH_2-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{P^+}}-Me\right]^+$$

in which the donor is now the nitrogen atom[384], presumably because the phosphorus is no longer in the trivalent state. Coordination to the nitrogen also occurs with the adducts of the compound $P(CH_2NEt_2)_3$, in this case presumably because of steric crowding of the trivalent phosphorus atom.[385] But no bonding to the nitrogen is found in the adducts of Me_2NPMe_2 and $(Me_2N)_2PMe$, in which the BH_3 links itself to the phosphorus only.[385]

Polydentate amines normally give adducts with more than one BH_3 group, as does, for example, N,N,N′,N′-tetramethylethylenediamine (TMED), $Me_2NCH_2CH_2NMe_2$. The bis adduct is sufficiently stable to be substituted in stages[386]:

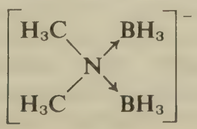
$$\mathrm{TMED.(BH_3)_2} \xrightarrow{2HX} \mathrm{TMED.(BH_2X)_2} \quad [X = F, Cl, Br]$$

With HBr the reaction proceeds further to give $\mathrm{TMED.(BHX_2)_2}$. Bis(dimethylamino)-methane likewise gives the bis-borane adduct $CH_2(NMe_2)_2.2BH_3$[387], while with methylated polyamines such as pentamethyldiethylenetriamine there is a quantitative addition of one BH_3 group per nitrogen atom with excess B_2H_6.[388] However, controlled conditions with polyamines can lead to adducts with less than the maximum proportion of borane, as with



which give both the 1:1 and 1:2 adducts with BH_3.[389] It has been shown that, with fully substituted nitrogen in a ring, isomeric BH_3 adducts are formed: in the case of 1-methyl-2-substituted piperidines the axial isomers are preferred.[390] With hexamethylenetetramine adducts containing 1, 2, 3 and 4 BH_3 groups respectively are formed.[391]

The possibility of two BH_3 groups becoming linked to the same nitrogen atom only arises if the latter is negatively charged. Thus the ion



is isoelectronic with $Me_3N.BH_3$. The sodium salt can be formed by the interaction of μ-dimethylaminodiborane with sodium tetrahydroborate[392]

$$\mu\text{-}Me_2NB_2H_5 + NaBH_4 \rightarrow Na[Me_2N(BH_3)_2]$$

Adducts with Amine Derivatives Substituted at the Nitrogen

The powers of forming borane(3) adducts are somewhat reduced if the nitrogen is substituted by silyl groups instead of alkyl groups. Like carbon, silicon has no lone pairs of electrons, so that a reason must be sought in its lower electronegativity. Possibly steric effects also play a role. Thus trisilylamine $N(SiH_3)_3$ does not form a BH_3 adduct[393], while the silyl bases $NMe(SiH_3)_2$ and NMe_2SiH_3 give simple adducts with the BH_3 group attached to the nitrogen.[394] However, these adducts are appreciably less stable thermally than $H_3B.NMe_3$ and split off silane SiH_4 at 0°C. Bis(dimethylamino)silane gives the bis-borane adduct $SiH_2(NMe_2.BH_3)_2$, but probably for steric reasons $SiH(NMe_2)_3$ and $Si(NMe_2)_4$ give only the 1:2 and 1:1 borane adducts respectively.[387]

A new situation arises when there is a substituent on the nitrogen that itself has one or more lone pairs of electrons, as when the nitrogen is linked to a Group-V or Group-VI atom. In such cases there is competition between the lone pairs for the BH_3 group, and only in certain instances are adjacent donor atoms simultaneously satisfied with the formation of bis-borane adducts. A case in point is hydrazine H_2NNH_2 (p. 25).

When the nitrogen atom is directly linked to an atom of phosphorus, arsenic or, for that matter, sulphur, only the mono adduct of BH_3 is formed. In such a case the boron is linked to the phosphorus, arsenic or sulphur, respectively (pp. 32, 37), and the nitrogen does not act as donor. But the nitrogen probably does participate in coordination to BH_3 when the adjacent element is oxygen. Only nitrogen compounds containing alkoxy and similar groups come into question here, however, since OH groups react too readily in other ways with B_2H_6 (and hence BH_3). The simplest compounds are those formed by hydroxylamine and its derivatives. Although reaction with B_2H_6 is liable to proceed explosively, at sufficiently low temperatures it is possible to form BH_3 adducts. The adducts of NH_2OH and $NHMeOH$ are particularly unstable and lose hydrogen below room temperature, apparently undergoing internal oxidation, to give inadequately characterized products; but $H_3B.NMe_2OH$ is appreciably more stable thermally and, under reduced pressure, can be distilled at 25°C, even though it starts to decompose just above 30°C.[395] However, it reacts destructively with excess B_2H_6, and its B—N bond is moreover apparently rather weak, because the NMe_2OH can be replaced by NMe_3. The O-methyl derivatives of hydroxylamine give BH_3 adducts of enhanced stability.[396] Both $H_3B.NH_2OMe$ (m.p. 55°C) and $H_3B.NHMeOMe$ (m.p. -23 – -21°C) split off hydrogen if gently warmed and explode violently through hydride-methoxy transfer if rapidly heated to 90°–100°C. They are only slightly volatile at room temperature, but $H_3B.NMe_2OMe$ has a much greater volatility (v.p. 3·8 Torr at 26°C) and is also more stable, losing hydrogen only on stronger heating. Again, heating these compounds leads to internal oxidation resulting in products in which the methoxy groups have been transferred to the boron.

It is not known whether fluoramide NH_2F, fluorimide NHF_2, or their alkyl derivatives form BH_3 adducts, but it has been stated that NF_3 does not.[207] It is in any case clear that the N—F bond is attacked by diborane(6) at elevated temperatures.[397] The N—Cl bond of dimethylchloramine Me_2NCl is attacked at room temperature even by coordinated BH_3[351]; no BH_3 adduct is known, and reduction to dimethylamine occurs.

Hydrazine Boranes

Hydrazine N_2H_4 forms a 1:1[181,398] and a 1:2[180–1] adduct with BH_3 at low temperatures, as do methylhydrazines.[180,399,182] Whereas for a long time it was not known whether hydrazine behaved like ammonia to cleave diborane asymmetrically, the recent proof[400] that hydrazine borane $H_3B.N_2H_4$ is isosteric with $C_2H_5NH_2$ establishes that the cleavage by hydrazine is symmetric. The measured standard enthalpies of formation of the crystalline mono- and bis-borane(3) adducts of N_2H_4 are $-10{\cdot}8 \pm 0{\cdot}7$[401]

and $-22{\cdot}2 \pm 0{\cdot}8$[402] kcal mol^{-1} respectively, though rather different values have also been reported.[403] The length of the B—N bond in $H_3B.N_2H_4$ is 1·56 Å.[400] The ^1H, ^{11}B and ^{14}N n.m.r. spectra of $H_3B.N_2H_4$ in liquid hydrazine have been reported.[404–7] The compound undergoes hydrogen exchange with the solvent, and also forms a hydrogen bond with one molecule of solvent via one of the hydrogen atoms linked to the nitrogen atom coordinated to boron. For the bis adduct $N_2H_4.2BH_3$ the infrared spectrum has been recorded.[408] These compounds are very unstable and lose hydrogen at and above room temperature, that is, more readily than does $H_3B.NH_3$. The kinetics of decomposition of $H_3B.N_2H_4$ have been studied over the temperature interval 29·5°–57°C.[409] No free radicals are involved, and the first step is

$$H_3B.NH_2NH_2 \rightarrow H_2BNHNH_2 + H_2$$

(though, by analogy with $H_3B.NMe_2H$, it is probably not unimolecular[348]); subsequent steps lead to the formation of $(H_2BNHNHBH_2)_n$, isolable at 57°C.[409] First-order rate constants have been determined for the decomposition of $H_3B.N_2H_4$[410] and $H_3B.NH_2NH_2.BH_3$.[411]

In the event that one of the nitrogen atoms is substituted further, the question that arises concerns which nitrogen atom becomes linked to the boron on forming the monoborane(3) adduct. In the case of $H_3B.N_2H_3Me$, both isomers have been reported, the more abundant being $H_3B.NH_2NHMe$.[412] Its thermal decomposition is complex, being a combination of zero-order and first-order mechanisms over the temperature range 65°–90°C. The mono adduct with 1,1-dimethylhydrazine, $H_3B.N_2H_2Me_2$, has been investigated by infra-red, Raman and n.m.r. spectroscopy[413–4], but the two groups of workers concerned draw opposite conclusions regarding whether the structure is $H_3B.NMe_2NH_2$ or $H_3B.NH_2NMe_2$. (The fact that the boron is linked to the NH_2 group of NH_2NMe_2 in the trimethylborane(3) adduct[415] is no safe criterion, since steric factors doubtless play a stronger role there.) Later workers[416] favour the structure $H_3B.NH_2NMe_2$. The solid compound decomposes by a first-order molecular mechanism at 30°–45°C, whereas the melt at 70°–95°C decomposes by an ionic mechanism that has zero-order and first-order components.[416] The bis-borane adduct $H_3B.NH_2$-$NMe_2.BH_3$, however, has a pyrolysis mechanism which is strictly first order in both the solid and liquid phases.[417]

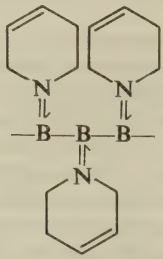
Tetramethylhydrazine also gives a bis adduct; but although it has been claimed that $N_2H_4.2BH_3$ loses hydrogen on heating without appreciable rupturing of the N—N bond[398], the N—N bond is not preserved when $N_2Me_4.2BH_3$ is heated.[182] In this case N,N-dimethylboranamine H_2BNMe_2 (or its dimer) and hydrogen are formed:

$$Me_4N_2.2BH_3 \xrightarrow{100°C} 2Me_2NBH_2 + H_2$$

Adducts with Compounds of Multiply Bonded Nitrogen

Compounds in which nitrogen is linked to another element by a multiple bond do not easily give adducts because the multiple bond is too readily reduced by a hydroboration reaction (p. 100). However, triple bonds are less readily attacked than double bonds. Since, as measured by the change in its vibrational frequency, the C≡N bond of alkyl cyanides on coordination with BF_3 is strengthened[418], in contrast to the C=O bond of ketones[419], this might provide at least a partial explanation, if it can be assumed that the changes on coordination with BH_3 are qualitatively similar. The adduct with hydrogen cyanide, $H_3B.NCH$, is unknown, but has been treated theoretically.[420] On the other hand, that with acetonitrile, $H_3B.NCMe$ (Table VI), has been successfully prepared as a solid that possesses a moderate stability below room temperature; but if stored at 20°C it turns liquid within 6 days through decomposition.[199] The compounds $H_3B.NCSiH_3$ and $H_3B.NCSiMe_3$ can also be formed, but if heated lose SiH_4 and $SiHMe_3$ respectively to leave a solid of empirical formula BH_2CN.[421] Adducts of metal complexes containing cyano groups are also possible: in π-cyclopentadienyldicarbonylcyanoiron(II) borane $(\pi\text{-}C_5H_5)Fe(CO)_2CN.BH_3$ the boron is linked to the nitrogen.[422] The ionic complex $[H_3B.NC]^-$ can be formed, but its rather ready transformation in tetrahydrofuran solution to the isomeric $[H_3B.CN]^-$ ion is catalyzed both by acids and the CN^- ion.[293] It has been subjected to spectroscopic[195] and theoretical studies.[193,195,270] Borane(3) complexes of the $C(CN)_3^-$ [298], $N(CN)_2^-$ [298], N_3^- [423], and CNO^- [298] ions are also known, though some of the complexes are unstable and undergo chemical change. In the last case it is not known whether the boron is linked to the nitrogen.

Again, if the nitrogen is bound in an unsaturated heterocyclic ring, attempts to isolate the BH_3 adduct are likely to lead to preferential reduction, but not if the ring is truly aromatic, which gives it an added stability. Thus reduction of the 5-membered ring in indoles is liable to occur, although BH_3 adducts are first formed[424]: no reduction occurs with N-substituted indoles. However, pyridine is not reduced and gives the stable adduct $H_3B.NC_5H_5$ (Table VI), m.p. 10°–11°C.[170] The pyridine can be displaced by trimethylamine,[170] and the phase diagram reveals no sign of any interaction between $H_3B.NMe_3$ and C_5H_5N.[425] If heated to 120°C, $H_3B.NC_5H_5$ undergoes ring hydrogenation to give a chain polymer of structure[426]



A little above 150°C, a violent reaction sets in. With NMe_2Cl pyridine borane does not give the expected compound $[H_2B(NHMe_2)Py]Cl$, but $[H_2BPy_2]Cl$ and $[H_2B(NHMe_2)_2]Cl$ by disproportionation.[351] The borane(3) adduct of 4-methylpyridine is readily converted by CPh_3Cl to $4\text{-}MeC_5H_4N.BH_2Cl$ and $4\text{-}MeC_5H_4N.BHCl_2$.[378] The ultraviolet photoelectron spectra of several 4-substituted pyridine boranes have been studied.[427] No evidence of interaction between the π system of the pyridine ring and the π component of the BH_3 group was found. The structure of the adduct of BH_3 with poly(4-vinylpyridine) has been investigated.[404]

The boron is also linked to nitrogen in the boranonitrite ion $[N(O).BH_3]^-$, which is isoelectronic with the nitrite ion: it is prepared by the action of B_2H_6 on a hyponitrite.[428] The neutral adduct borane nitrosyl, $H_3B.NO$, is however not isolable, although mass-spectrographic evidence for a short-lived molecule of that formula has been obtained.[280]

ADDUCTS WITH COMPOUNDS OF PHOSPHORUS, ARSENIC AND ANTIMONY

General

Numerous adducts of borane(3) with compounds of trivalent phosphorus are known. Because their stability is surprisingly high, relatively speaking, there has been much discussion in the scientific literature concerning the nature of the B—P bond in these compounds. For this reason, some preliminary remarks of a general nature are required here before proceeding to treat individual compounds.

Although the enthalpies of reaction of a number of phosphines with diborane(6) have been measured[429], because of lack of information concerning the heats of sublimation and solution of the products no precise numerical comparison of the strengths of boron-phosphorus and boron-nitrogen bonds can be given at present; but for every analogous pair of phosphine and amine boranes so far studied, the phosphorus compound has the lower degree of dissociation. For example, trimethylphosphine borane(3) $Me_3P.BH_3$ is reported to be essentially undissociated in the vapour phase at 200°C.[192] Also it is stated that the assumed equilibrium

$$Me_3N.BH_3(s) + Me_3P(g) \rightleftharpoons Me_3P.BH_3(s) + Me_3N(g)$$

lies well over to the right[192], since the amine is displaced by the corresponding phosphine[374]; but it is questionable whether one can speak of a true equilibrium here because it is not feasible to displace the phosphine completely by the amine even with excess of the latter, and attempts to do so result in the formation of other compounds in which the boron still remains linked to phosphorus[430–1], e.g.

$$2H_3P.BH_3 + NH_3 \rightarrow NH_4[PH_2(BH_3)_2] + PH_3$$

The fact that the B—P bonding in the simple phosphine boranes is stronger than would be expected for σ bonding alone[432] has evoked considerable discussion, and it has frequently been suggested that additional π bonding involving the 3*d* orbitals of the phosphorus is present.[202] However, there is no unambiguous evidence to support this suggestion. Rather, recent theoretical considerations imply that if there is π bonding in $H_3P.BH_3$, the effect must be small.[433–4] Moreover, π bonding would cause shortening of the P—B bond, but in $Me_4P_2.2BH_3$ its length is 1·951 Å, which is actually 0·124 Å *longer* than the single P—C bond in the same compound.[183] Also the barrier to internal rotation about the B—P bond in $H_3P.BH_3$ is only 2·47 kcal mol^{-1} [435], which is hardly compatible with appreciable π bonding and is exactly the same as the value calculated for the B—N bond in $H_3N.BH_3$.[324] Further, the marked shift in the B—H stretching frequencies which would be expected from π bonding is not observed, there being but a slight difference in the frequencies for $Et_3P.BH_3$ and $Et_3N.BH_3$.[216] Other arguments against π bonding have been voiced.[194]

A clue to the true state of affairs doubtless lies in the observation of Burg, who noted that the P—H stretching frequencies in the phosphines increase on coordination to borane[436], which is the opposite effect of that observed with the N—H stretching frequencies of amines. This implies that additional energy is liberated by the three phosphine bonds on coordination of the phosphorus atom, hence increasing the reaction energy, whereas with amines it is depressed. These effects will account for a large part if not all of the enhancement in coordination energy observed with phosphines (relative to amines). In other words, the anomalous trend in the dissociation energies of the B—N and B—P bonds could be compatible with a normal trend in the true or intrinsic bond energies as reflected by other bond properties. The stretching force constants do in fact support this explanation and show the normal trend, having been calculated as 4·56 mdyne Å^{-1} for the B—N bond in $H_3N.BH_3$[313] and 1·958 or 1·97 mdyne Å^{-1} for the B—P bond in $H_3P.BH_3$.[437–8] The point warrants further investigation, but it is already apparent that there is no clear case for supplementary π bonding in the phosphine boranes.

The nature of the P—B bond in BH_3 complexes of phosphines has been studied by n.m.r. techniques[439–40], and it has thereby been confirmed that it is a true coordination bond. Even if the effect is not excluded, the n.m.r. evidence is inconsistent with BH_3 hyperconjugation in these compounds.[441] There is however a correlation between the ^{31}P–^{11}B coupling constant on the one hand and the phosphine base strength[441] or P→B dative bond strength[442] on the other. Possible correlations involving chemical-shift data have also been studied.[443] Other techniques which have been applied to the problem include magneto-optical, magnetic susceptibility[221] and molecular refraction studies.[220–2, 444]

Phosphine boranes are very readily prepared, most easily by reacting the phosphine directly with diborane(6). Arsine boranes can be prepared similarly. In the case of the phosphine boranes, at least, a useful alternative is to react the base with $NaBH_4$ plus iodine in a polyether such as monoglyme[310, 445]

$$2PR^1R^2R^3 + 2NaBH_4 + I_2 \xrightarrow[\text{polyether}]{25°C} 2NaI + 2H_3B.PR^1R^2R^3 + H_2$$

—reaction ingredients which are known to produce B_2H_6 *in situ*.[446] Another method is to displace the base from an amine borane or borane carbonyl in an exothermic reaction:

$$H_3B.NR'_3 + PR_3 \rightarrow H_3B.PR_3 + NR'_3$$

With tri-*n*-butylphosphine the displacement of the amine has been shown to proceed mostly by a second-order S_N–2B reaction.[375–6]

Alternatively the acidic moiety of a B-substituted phosphine borane may be displaced by the use of $LiBH_4$[447]

$$BCl_2(OEt).PEt_3 \xrightarrow[C_4H_8O\ (20°C)]{LiBH_4} H_3B.PEt_3$$

Phosphine Borane

The simplest of the phosphine adducts of borane(3) is phosphine borane $H_3B.PH_3$, which was (in 1940) also the first to be discovered.[201] At first suspected to be the dimer $B_2H_6.2PH_3$, it has since definitely been shown to be monomeric.[200, 448] Its formation from gaseous phosphine and diborane(6) at room temperature is slow, and it is reported that the following mechanism, though not unique, is compatible with a kinetic study[449]:

$$B_2H_6 + PH_3 \rightleftharpoons H_3B.PH_3 + BH_3$$
$$BH_3 + PH_3 \rightleftharpoons H_3B.PH_3$$

Ethers however catalyze the reaction very markedly, and to react the gases in monoglyme or diethyl ether solution at low temperatures[214] is for certain purposes not requiring isolation of the product a more convenient method of production. The compound is a very volatile solid (v.p. 200 Torr at 0°C[201]), which can readily be dissociated back into the starting materials, but it melts in a sealed tube at 32°–33°C without noticeable decomposition to give a normal monomeric liquid.[200] Microwave studies of $H_3B.PH_3$ (16 isotopic species) have established the structure with high precision, as well as the dipole moment and the height of the potential barrier to internal rotation[435] (see Table X). The conformation is staggered, and the angles at the boron and especially the phosphorus depart appreciably from the tetrahedral angle. Infra-red and n.m.r. spectra have been reported[450], as have the Raman frequencies.[438, 451] The B—P bond order has been calculated from earlier spectroscopic data to be 0·78.[437] The molecule has also been the subject of various theoretical treatments.[195, 329, 433, 452–5]

Table X.—Miscellaneous Molecular Properties of Phosphine Borane(3)[(a)]

Parameter	Species	Value
Interatomic distance (Å)	P—B B—H P—H	1·937 ± 0·005 1·212 ± 0·002 1·399 ± 0·003
Interbond angle	H—B—H P—B—H H—P—H B—P—H	114° 36 ± 12′ 103° 36 ± 12′ 101° 12 ± 12′ 116° 54 ± 12′
Dipole moment (D)	$H_3B.PH_3$	4·00 ± 0·03
Barrier to internal rotation of BH_3 group (kcal mol^{-1})	$H_3B.PH_3$	2·467 ± 0·050

[(a)] Ref. 435.

Probably because of the volatility and rather ready dissociation of $H_3B.PH_3$, its chemistry has received but slight study. At 35°C it does not undergo deuterium exchange at the boron or the phosphorus.[450] That the hydrogen attached to the phosphorus is more acidic than that attached to the boron, is apparent from its reactions, including that with *n*-butyllithium[456]

$$H_3P.BH_3 + C_4H_9Li \xrightarrow[Et_2O]{-20°C} C_4H_{10} + Li^+[H_2PBH_3]^-$$

lithium phosphinotrihydroborate(1−)

The B—P bond is strengthened and the BH_3 group remains intact, as it does in the reaction with $NaBH_4$[457] or NH_3[430] to give a bisboranohypophosphite:

$$H_3P.BH_3 + NaBH_4 \xrightarrow{0°C} Na[H_2P(BH_3)_2] + H_2$$

$$2H_3P.BH_3 + NH_3 \xrightarrow{-45°C} NH_4[H_2P(BH_3)_2] + PH_3$$

Infra-red, Raman and n.m.r. spectra of the isotopically substituted anion have been reported.[458] In such anions the BH_3 group acts as a ligand isoelectronic with an oxygen atom, as it does elsewhere (pp. 17, 26). With phosphorus, the number of BH_3 ligands can be increased to 3 and 4 to give a trisboranophosphite and tetrakisboranophosphate respectively by the use of B_2H_6 and *n*-butyllithium[459]:

$$Li[H_2P(BH_3)_2] + C_4H_9Li + \tfrac{1}{2}B_2H_6 \rightarrow Li_2[HP(BH_3)_3] + C_4H_{10}$$

$$Li[HP(BH_3)_3] + C_4H_9Li + \tfrac{1}{2}B_2H_6 \rightarrow Li_3[P(BH_3)_4] + C_4H_{10}$$

N.m.r. studies have shown that with increasing substitution the chemical shifts of the protons bonded to the phosphorus exhibit a profound and progressive change, whereas those of the BH_3 protons are little affected with respect to the value found for $H_3P.BH_3$.[459] The anions do not however require to be made from $H_3P.BH_3$, since they can also be prepared from a metal phosphinide[460] or from a phosphonium salt[458, 461]:

$$KPH_2 + B_2H_6 \xrightarrow[Et_2O]{-78°C} K[H_2P(BH_3)_2]$$

$$PH_4I + 2NaBH_4 \xrightarrow[\text{monoglyme}]{-78°C} Na[H_2P(BH_3)_2] + NaI + 2H_2$$

$KPMe_2$ likewise gives $K[Me_2P(BH_3)_2]$.[460] The products are very reactive, and react with HCl or O_2 at room temperature. In all the foregoing reactions of $H_3P.BH_3$ the BH_3 group remains intact, but HCl successively replaces the hydrogen in the borane moiety of $H_3P.BH_3$ to give $H_3P.BH_2Cl$, $H_3P.BHCl_2$ and $H_3P.BCl_3$ in identifiable steps of the type[201]

$$H_3P.BH_3 + HCl \rightarrow H_3P.BH_2Cl + H_2$$

Adducts with Substituted Phosphines, Arsines and Stibines

For substituted phosphines the stability of the borane(3) adduct tends in most cases to increase with progressive substitution of the hydrogen by organic or other groups. The relatively high stability of $H_3B.PMe_3$ has already been noted (p. 26). On the other hand, borane(3) shows a progressively decreasing tendency to form a stable adduct with an arsine or stibine. Thus arsine borane $H_3B.AsH_3$ is not isolable, but again as the arsine is progressively methylated adducts of increasing stability are formed.[208] Apart from $H_3B.SbMe_3$, which is very unstable and decomposes at −35°C[209], adducts of alkylated stibines and bismuthines are not known. In part, no doubt, this is also because B_2H_6 (and hence BH_3) readily reduces the bases at the Sb—C and Bi—C bonds, as it does with the triphenyl derivatives.[462]

In general, the stability of the borane complex of a phosphine or arsine is exceptionally sensitive to the nature of the substituents attached to the Group-V atom, since these affect not only the Lewis base strength, but also the steric requirements of the base. Any change which increases the *p* character of the lone pair on the donor atom or permits a closer approach of the boron atom will tend to strengthen the interaction. A case in point is the stabilization of the complex of tricyclopropylphosphine, $(c\text{-}C_3H_5)_3P.BH_3$, relative to that of triisopropylphosphine, $(i\text{-}C_3H_7)_3P.BH_3$.[463]

N.m.r. techniques applied to the study of the B—P bond[439–40] reveal that in benzene solution at room temperature $H_3B.PMe_3$ does not undergo intermolecular exchange reactions with excess of the starting materials. This parallels the behaviour of $H_3B.NMe_3$.[371]

As reported for the amine boranes (p. 21), boranes of substituted phosphines and arsines may be prepared by reacting the phosphine or arsine with gaseous diborane(6) direct, or with B_2H_6 prepared *in situ*[446] in a polyether solution from $NaBH_4+I_2$.[310] Alternatively they may be prepared from an amine borane by simply substituting the amine by a phosphine in an exothermic reaction.

$$H_3B.NR'_3+PR_3 \rightarrow H_3B.PR_3+NR'_3$$

With tri-*n*-butylphosphine such displacements have been shown to proceed mostly by a second-order S_N-2B reaction.[375–6] Methylphosphine borane(3) $H_3B.PH_2Me$ has been similarly formed by displacing carbon monoxide from borane(3) carbonyl[279]

$$H_3B.CO+PH_2Me \rightarrow H_3B.PH_2Me+CO$$

It melts at *c.* −49°C and has a vapour pressure of 3·5 Torr at 23·6°C.[202] The structure of $H_3B.PH_2Me$ has been very precisely ascertained by microwave studies.[464] Infrared and Raman studies have provided a P—B stretching force constant of 2·44 mdyne $Å^{-1}$ and barriers to internal rotation of the BH_3 and CH_3 groups of 1·57 and 2·49 kcal mol^{-1} respectively.[465] These figures indicate a marked strengthening of the P—B bond relative to that in $H_3B.PH_3$ (p. 28) without the introduction of any π bonding. The $H_3B.PH_2Me$ molecule has been investigated by the CNDO/2 approximation.[466] The rather more stable dimethylphosphine borane $H_3B.PHMe_2$ melts at −22·6°C and has a vapour pressure of 2·36 Torr at 29·5°C.[202] It has been thoroughly investigated by microwave, infrared and Raman spectroscopy.[467] Progressive methylation at the phosphorus is accompanied by a marked reduction in the P—B bond length in addition to the increase in stretching force constant mentioned above. N.m.r. studies have also been reported[468–9], and the regular trend in the value of the coupling constant $^1J_{PB}$ with methylation at the phosphorus commented upon.[442] Work with the trideuteroborane(3) analogue has indicated the absence of H-D exchange at the boron.[469] Progressive methylation at the phosphorus also brings about a regular increase in the dipole moment, since the values for $H_3B.PH_2Me$, $H_3B.PHMe_2$ and $H_3B.PMe_3$ are reported as 4·58, 4·78 and 4·97 D respectively.[470] A molecular-orbital study of the dipole moments has been carried out.[329] Other alkyl[439] and phenyl[432] analogues have been characterized, as has the cyclic secondary phosphine adduct $H_3B.PH(CH_2)_4$,[471] which melts at *c.* −65°C and shows no dissociation at temperatures up to 150°C.

Phosphine boranes with hydrogen linked to the phosphorus lose molecular hydrogen on heating. Thus $H_3B.PH_2Me$ begins to evolve H_2 at 80°C and $H_3B.PHMe_2$ at 150°C, whereas, by contrast, $H_3B.PMe_3$ is stable at 200°C.[472] In the first two instances there is an analogy with primary and secondary amine boranes (p. 20), but the products are not the strict analogues of the boranamines (aminoboranes), since the phosphinoboranes are mixtures of oligomers of respective types $(HMePBH_2)_n$ and $(Me_2PBH_2)_n$,[202]

$$HMe_2P.BH_3 \xrightarrow[40h]{150°C} \frac{1}{n}(Me_2PBH_2)_n+H_2 \quad [n = 3, 4]$$

where n is usually 3 or 4 or a high number, whereas the boranamines are ordinarily oligomerized only to dimers or occasionally trimers (pp. 423–426). The trimeric and tetrameric phosphinoboranes are known to be cyclic.[473–4] The primary and secondary arsine boranes, however resemble the corresponding phosphorus compounds, but are less stable, have higher dissociation pressures, and commence to lose hydrogen at lower temperatures to give trimeric and tetrameric arsinoboranes. Thus $H_3B.AsHMe_2$, which is less stable than $H_3B.AsME_3$,[208] melts at −22·4 to −21·5°C, has a vapour pressure of 8·11 Torr at 0°C and evolves H_2 at 130°C.[208]

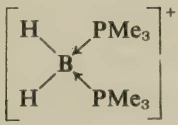
$$H_3B.AsHMe_2 \xrightarrow[36h]{130°C} \frac{1}{n}(Me_2AsBH_2)_n+H_2 \quad [n = 3, 4]$$

The reactions of these phosphine and arsine boranes have otherwise been little studied, but it is known that reaction with sodium hydride in ether results in a complex salt.[291]

$$H_3B.PHMe_2+NaH \xrightarrow{R_2O} Na[BH_3PMe_2]+H_2$$

The most stable adducts with BH_3 are in general formed by the tertiary phosphines or arsines respectively. Many such adducts have been characterized and their physical properties are mostly well known, including those of $H_3B.PMe_3$[202] and $H_3B.AsMe_3$[166, 208] (Table VI). Vibrational and n.m.r. spectra, and also enthalpies of formation, have been reported for $H_3B.PMe_3$, $H_3B.AsMe_3$ and $H_3B.SbMe_3$.[475] Additionally, the vibrational spectra of $D_3B.PMe_3$[476] and $D_3B.AsMe_3$[477] have been used to determine the structures of the trimethylphosphine and trimethylarsine adducts and calculate their P—B and As—B stretching force constants to be 2·37 and 1·84 mdyne Å^{-1} respectively. The n.m.r. spectrum of $H_3B.PEt_3$ has been reported[478], while for this and several other compounds of types $H_3B.PR_3$ and $H_3B.PHR_2$ [R = alkyl] comparison has been made of the magneto-optical properties of the B—H bonds and information obtained regarding rotation about the P—B bonds.[444] The barriers to internal rotation for the molecule $H_3B.P(t\text{-Bu})_3$ have also been determined.[479] The molecule $H_3B.PMe_3$ has been subjected to a theoretical conformational analysis[480], which assigns it a staggered configuration.

Chemically, the borane adducts of the fully alkylated phosphines and arsines do not exhibit any unexpected properties. The thermal decomposition (as distinct from dissociation) has been studied.[209] The principal volatile product is hydrogen, but the residues were not identified. Except for a very little methane from the PMe_3 and $AsMe_3$ derivatives, no alkanes were produced, so that decomposition to compounds of the type $(H_2BPR_2)_n$ and $(H_2BAsR_2)_n$ is not indicated here. On heating with diborane(6) or with 'onium' salts of large anions, $H_3B.PMe_3$ and $H_3B.AsMe_3$ readily give salts of the complex cations[481–2]



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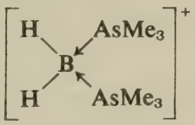


Otherwise little is known about the chemistry of the parent compounds, except that (at least in the case of the phosphine boranes) the borane moiety can be progressively halogenated by N-chlorosuccinimide or by boron trichloride[483]:

$$R_3P.BH_3 \xrightarrow{ClN(OCCH_2)_2} R_3P.BH_2Cl \xrightarrow{ClN(OCCH_2)_2} R_3P.BHCl_2$$

$$R_3P.BH_3 \xrightarrow{BCl_3} R_3P.BH_2Cl \xrightarrow{BCl_3} R_3P.BHCl_2$$

Triphenylphosphine borane $H_3B.PPh_3$ is preparable by the foregoing general methods or by pyrolyzing tetraphenylphosphonium tetrahydroborate[484]

$$[P(C_6H_5)_4][BH_4] \xrightarrow{heat} C_6H_6 + H_3B.P(C_6H_5)_3$$

It is a sublimable solid, m.p. 189°C.[432] The P—B bonding is less strong than in the adducts of the trialkylphosphines.[429] The stretching frequencies and the value of the dipole moment (4·79 ± 0·20 D) again here give no indication of π bonding between the boron and the phosphorus.[432] Some of the chemical properties have been studied: the borane group is removed by mercuric salts, which are in part reduced and in part form the compounds $Ph_3P.HgX_2$.[432] Exchange of the boron with that of diborane occurs in benzene solution,

$$Ph_3P.{}^{10}BH_3 + {}^{11}B_2H_6 \overset{C_6H_6}{\rightleftharpoons} Ph_3P.{}^{11}BH_3 + {}^{10}B{}^{11}BH_6$$

possibly via an unidentified B_3H_9 complex, and requires about 1 day at room temperature to establish equilibrium. The borane moiety can be completely brominated in identifiable steps through $Ph_3P.BH_2Br$ and $Ph_3P.BHBr_2$ by Br_2 in benzene or by BBr_3.[432] Bromination is also realized with HBr, and in the cases of the mixed methylphenylphine boranes $H_3B.PMe_nPh_{3-n}$ [n=0, 1, 2, 3] the trend in the reactivity correlates with the decrease in hydridic character of the B—H bonds, whether arising through reduced base strength of the phosphine or enhanced $d\pi$-$p\pi$ bonding between the phosphorus and the B—H bonds.[485]

Under mild conditions triphenylarsine has been shown to give $Ph_3As.BH_3$[462, 486], but no BH_3 adduct was obtained from $AsHPh_2$, $AsPh_2(SiMe_3)$, $AsPh_2(SnMe_3)$ or As_2Me_4.[486] Even under the mildest conditions no BH_3 adducts of Ph_3Sb and Ph_3Bi could be prepared because of reduction.[462]

In the BH_3 adducts of the substituted bases $Me_2PCH_2NMe_2$ and Me_2PCH_2SMe (the former also forms a bis adduct) the phosphorus is linked to boron[384], and is thus seen to be a stronger donor towards BH_3 than is nitrogen or sulphur.

Bis-borane adducts are formed by the biphosphines of type HPhP—R—PHPh[487] as well as by $Me_2PC_2H_4PMe_2$.[488] That from the latter decomposes on heating to a mixture of $(Me_2PBH_2)_3$ and $(Me_2PBH_2)_4$.

Adducts of phosphorus-containing ylides are of interest, that is, of compounds such as alkylidene triphenylphosphoranes, of which the simplest is $Ph_3P{=}CH_2$ or $Ph_3\overset{+}{P}—\bar{C}H_2$. This compound does not behave like the nitrogen analogue $Me_3\overset{+}{N}—\bar{C}H_2$ (p. 110), but gives a borane adduct which may be written as $Ph_3P{\rightarrow}CH_2{\rightarrow}BH_3$ or $Ph_3\overset{+}{P}—CH_2—\bar{B}H_3$.[299] The first product thus contains no boron-phosphorus link. It is stable towards water, but is a strong reducing agent. On refluxing in non-polar solvents it rearranges initially to $Ph_3\overset{+}{P}—\bar{B}H_2—CH_3$ and then to $Ph_3P.BH_3$ with the evolution of PPh_3 and BMe_3.[489] Adducts from analogues of the type $Ph_3\overset{+}{P}—\bar{C}HR$ have also been reported[300], while the ylide $Me_3Si\bar{C}(PMe_2)\overset{+}{P}Me_3$ forms a bis-borane(3) adduct.[490] A borane(3) adduct is also given by the arsenic-containing ylide $Me_3\overset{+}{As}—\bar{C}HSiMe_3$.[301]

Silyl-substituted and germyl-substituted phosphines also form typical borane(3) adducts, and even the simplest of them, $H_3SiPH_2.BH_3$[491, 21] and $H_3GePH_2.BH_3$[492], are not ionic. However, they will exchange hydrogen between the boron sites and the silicon or germanium sites respectively.[493, 492] The adducts $Si_2H_5PH_2.BH_3$ and $(H_3Si)_2PH.BH_3$ also exist and give $(PH_2BH_2)_n$ and $(PHBH)_n$ respectively with the liberation of a silane on heating.[494] Similarly $(Me_3Si)Et_2P.BH_3$ splits off $SiHMe_3$ > 80°C to leave $(Et_2PBH_2)_3$.[495] Unlike $(Me_3Si)_3N$, which does not react with B_2H_6[393], $(Me_3Si)_3P$ gives $(Me_3Si)_3P.BH_3$[203], m.p. 100°–107°C, which also eliminates $SiHMe_3$ on heating.[496]

Substituted phosphines with nitrogen linked directly to the phosphorus still give simple adducts with BH_3, in which the boron is attached to the phosphorus and never to nitrogen. The simplest of such nitrogen-containing substituents, the amino group $—NH_2$, is known in the compound $H_3B.P(NH_2)_3$, a crystalline solid first formed in the reaction of ammonia with trifluorophosphine borane[175]

$$6NH_3 + H_3B.PF_3 \xrightarrow[-111\,-\,+25\,^{\circ}C]{Et_2O} H_3B.P(NH_2)_3 + 3NH_4F$$

From X-ray structure analysis the P—B bond length is known to be $1{\cdot}887 \pm 0{\cdot}013$ Å.[497] The compound has been subjected to an LCAO-MO-CNDO/2 treatment and compared with the isoelectronic triaminophosphine oxide $OP(NH_2)_3$.[498] The structures of the methylated analogue tris(dimethylamino)phosphine borane $H_3B.P(NMe_2)_3$ (m.p. 32·5°, b.p. 49°–50°C), which has received a like theoretical treatment[499], and of other alkylated derivatives are comparable.[205, 222, 440, 500]

The formation of adducts of phosphines containing a sulphur substituent has been observed so far only in the cases of F_2PSMe and $FP(SMe)_2$.[501] Attempts to form an adduct of F_2PSPF_2 have led instead to the compound $H_3B.PF_2SSPF_2.BH_3$ with B_2H_6.[502] In every case the BH_3 group attaches itself to the phosphorus only.

Adducts with Diphosphines

Diphosphines mostly give bis adducts with BH_3, in contrast to compounds of type $R_2PNR'_2$, which are only capable of forming mono adducts. The simplest example is diphosphine P_2H_4, which with diborane(6) apparently gives the bis-borane(3) adduct $P_2H_4.2BH_3$, although this was originally cited as $P_2H_4.B_2H_6$.[503] The much better characterized $Me_4P_2.2BH_3$, which has three conformational isomers of known structure[183], can be recrystallized from petroleum ether, melts with slight decomposition at

194°C[488], and is completely decomposed by prolonged heating at a slightly higher temperature[182]

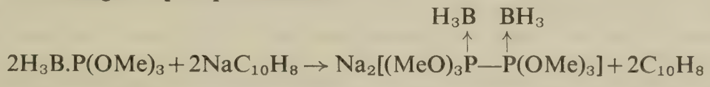
$$Me_4P_2.2BH_3 \xrightarrow[16h]{220°C} 2Me_2PBH_2+H_2$$

(The Me_2PBH_2 is recovered as a mixture of the trimer and tetramer.) In the bis adduct $(Me_2N)_4P_2.2BH_3$ the boron is again linked to the phosphorus[186], as is also true of the adducts of the phosphorus methylimide $P_4(NMe)_6$, which coordinates respectively to 1, 2, 3 or 4 BH_3 groups, as has been demonstrated by n.m.r. studies.[185] The fluoride P_2F_4 is readily converted by diborane(6) to the mono adduct $F_4P_2.BH_3$[504], while the unstable bis adduct $F_4P_2.2BH_3$[505], which commences to decompose at 0°C, has only been prepared by the use of H_3BCO at lower temperatures. The chloride P_2Cl_4 is reduced by diborane(6) to unidentified orange-yellow solids.[506] The compound Me_3PPCF_3 is unusual in that one of the phosphorus atoms has no lone pair: nevertheless it unexpectedly forms both a mono- and a bis-borane(3) adduct, the latter with both BH_3 units linked to the second phosphorus atom.[507]

Adducts with phosphites

Examples of substituted phosphines containing oxygen directly linked to the phosphorus are trialkyl phosphites $P(OR)_3$, which also readily give adducts of type $H_3B.P(OR)_3$.[206] Here, as with the BH_3 adduct of the mixed phosphine $Me(Et_2N)P(OCHMe_2)$[508], the boron is linked to phosphorus and never to oxygen.[220, 222, 440, 509–11] N.m.r. studies of the simplest member of the series $H_3B.P(OMe)_3$ (v.p. 23 Torr at 86°C), have been directed towards comparing the chemical shifts in CCl_4, C_6F_6 and C_6D_6 as solvents.[370] The coupling constant $^1J_{BP}$ for a number of adducts of mixed phosphines $H_3B.PXYZ$ [X, Y, Z = R, NMe_2, OR; R = alkyl] is not so good a criterion of stability of the complex as the heat of reaction of PXYZ with $\frac{1}{2}B_2H_6$.[512] The relative basicities of a number of phosphites have been determined by displacement-equilibrium studies and shown to fall in the order $PPh(OMe)_2 > P(OEt)_3 > P(OMe)_3 \geqslant P(OBu)_3 \sim P(OPh)_3$.[513] The relative basicity has also been shown to vary with the structure, and can be correlated with the B—H stretching frequencies.[514] However, for cyclic phosphites with 6-membered rings, the B—H frequencies for the borane(3) adducts indicate enhanced basicity for the axial lone pairs, whereas Lewis acids nevertheless appear to prefer the equatorial position.[515]

Little work has been done on the chemical properties of the borane(3) adducts of even the simple phosphites, but it is known that sodium naphthalide can bring about reduction to a charged diphosphorane derivative[516]



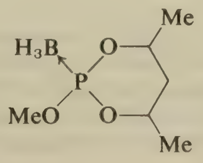
$$2H_3B.P(OMe)_3+2NaC_{10}H_8 \rightarrow Na_2[(MeO)_3\overset{\overset{H_3B}{\uparrow}}{P}—\overset{\overset{BH_3}{\uparrow}}{P}(OMe)_3]+2C_{10}H_8$$

On the other hand, N-bromosuccinimide attacks the borane moiety, which is brominated in identifiable stages[517]:

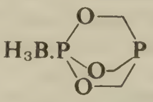
$$(MeO)_3P.BH_3 \xrightarrow{BrN(OCCH_2)_2} (MeO)_3P.BH_2Br \xrightarrow{BrN(OCCH_2)_2} (MeO)_3P.BHBr_2 \xrightarrow{BrN(OCHH_2)_2} (MeO)_3P.BBr_3$$

The accompanying change in the n.m.r. spectrum has been followed.

The precise geometry of the adduct schematically represented as



and involving the cyclic phosphite 2-methoxy-*cis*-4,6-dimethyl-1,3,2-dioxaphosphorinan has been established.[518] It has also been established that cyclization reduces the basicity of phosphite phosphorus.[515] However, towards BH_3 it still shows a stronger basicity than does phosphine phosphorus, since with the bicyclic phosphite $P(OCH_2)_3P$ the BH_3 unit links itself to the phosphite phosphorus in the mono adduct[519]



Adducts with Phosphorus(III) Oxide

With P_4O_6 borane(3) can function in much the same way as an oxygen atom to give compounds[520–2] that bear some formal resemblance to P_4O_{10}, namely $P_4O_6.BH_3$, $P_4O_6.2BH_3$, $P_4O_6.3BH_3$ and $P_4O_6.4BH_3$, though each successive BH_3 group is held less tenaciously than the former, so that the third compound has a low stability and the existence of the fourth is only demonstrable by equilibrium measurements in solution.[522]

Adducts with Phosphorus(III) and Arsenic(III) Halides

Phosphorus-halogen links in a phosphine do not prevent the formation of borane(3) adducts. Indeed, in spite of its generally weak Lewis-base powers, PF_3 was found to give with B_2H_6 under pressure the unexpected adduct $H_3B.PF_3$, which in physical properties and in stability resembles $H_3B.CO$ to a remarkable degree.[207] In this it is unlike NF_3, which forms no BH_3 adduct. The compound $H_3B.PF_3$ (Table VI) is monomeric and has a normal boiling point of −61·8°C. Its more important molecular parameters are known from microwave studies[523] and are reproduced in Table XI, together with the values for some other molecular properties. Other techniques which have been applied to study $H_3B.PF_3$ and (in part) $D_3B.PF_3$ are Raman[451,524–5], infra-red[451,524], n.m.r.[441,526] and photoelectron studies.[196] The B—P bond order has been calculated

Table XI.—Miscellaneous Molecular Properties of Trifluorophosphine Borane(3)

Parameter	Species	Value
Interatomic distance (Å)	B—H B—P P—F	1·207+0·006(a) 1·836±0·012(a) 1·538±0·008(a)
Interbond angle	H—B—H F—P—F	115±1°(a) 99° 50′±1°(a)
Dipole moment (D)	$H_3B.PF_3$	1·64±0·02(a)
Barrier to internal rotation about B—P axis (kcal mol⁻¹)	$H_3B.PF_3$	3·240±0·150(a)
Dissociation energy $D(H_3B—PF_3)$ at 25°C (kcal mol⁻¹)	$H_3B.PF_3$	$10{\cdot}99+\frac{1}{2}D(H_3B\cdots BH_3)$(b)
Ionization potential (eV)	$H_3B.PF_3$	11·02(c)
Stretching force constant (mdyne Å⁻¹)	B—H B—P P—F	3·202(d); 3·24(e) 2·295(d); 2·46(e) 6·124(d); 5·94(e)

(a) Ref. 523
(b) Calculated in Ref. 523 from the data in Ref. 207
(c) Ref. 196
(d) Ref. 437
(e) Ref. 524

from the vibrational spectra to be 0·92.[437] The bond dissociation energy at 25°C is equal to $\frac{1}{2}D(H_3B\cdots BH_3)+10{\cdot}99$ kcal mol^{-1}.[523]

Here again, theoretical calculations indicate that the P—B bond is essentially σ with little (if any) contribution from π bonding.[193, 195, 434, 454, 524, 527–8]

Chemically, the adduct $H_3B.PF_3$ has been studied with respect to its dissociation[207] and the effect thereon of excitation with an infra-red laser[529–30], as well as with respect to its PF_3-displacement equilibrium with PH_3.[531] Its reaction with oxygen has also been investigated.[532]

No borane(3) adduct of AsF_3 has been reported.

A further example of the importance of changes in the phosphine molecule itself, and one which also supports tentative conclusions mentioned earlier (p. 27), is provided by the anomalous stability of $H_3B.PHF_2$ [526], which is more stable than either $H_3B.PH_3$ or $H_3B.PF_3$. The anomaly has been ascribed to FHF interactions, and here we remark that any increase in such interactions on coordination of the phosphorus atom would enhance the reorganization energy liberated and thus stabilize the complex. Ligand repulsion, however, will provide at best a qualitative explanation.[533] The precise molecular structure of $H_3B.PHF_2$ has been established by microwave studies of the compound and several isotopic species.[534] Within experimental error the P—B interatomic distance is the same as that in the PF_3 complex, though the BH_3 group is no longer symmetrical and is also slightly tilted away from the fluorine atoms, and also the barrier to internal rotation is higher ($4{\cdot}0\pm0{\cdot}5$ kcal mol^{-1}). The dipole moment as given by Stark splittings is $2{\cdot}504\pm0{\cdot}030$ D[534], that is, higher than that of $H_3B.PF_3$. Vibrational[535] and n.m.r.[526] spectra have been recorded and the coupling constant $^1J_{PB}$ related to the dative bond strength.[442] Theoretical treatment of $H_3B.PHF_2$ by the CNDO/2 approximation leads to a slightly higher electron contribution from the phosphorus atom in the direction of the boron atom.[528] There are reasons for expecting the BH_3 moiety to occupy a tilted position.[455]

The structure of the related compound $H_3B.PMeF_2$ has also been determined by microwave measurements, and the dipole moment shown to be $3{\cdot}95\pm0{\cdot}05$ D.[536] Again the phosphine moiety is a strong base towards BH_3, but in this instance the base strength is not reflected in the value of the $^1J_{PB}$ coupling constant for the complex.[501] The interest associated with the anomalous base strengths of difluorophosphines has led to the preparation and study of the vinyl and propynyl analogues, $H_3B.PViF_2$[537], and $H_3B.P(C{\equiv}CMe)F_2$,[538] both of which show an enhanced stability. The base $F_2PCH_2CH_2PF_2$ coordinates at both phosphorus atoms to give a bis-BH_3 adduct, as confirmed by n.m.r. and infra-red studies.[539] The highly volatile and unstable adducts $H_3B.P(CF_3)_{3-n}F_n$ $[n=1,2]$[540] have also been formed, in spite of the particularly weak basic powers of $P(CF_3)_2F$, in which the fluorine atom attached to the phosphorus has enhanced reactivity. Accordingly this fluorine readily migrates to the boron at elevated temperatures or even at 0°C, whereby BHF_2, BF_3, $PH(CF_3)_2$, $[H_2BP(CF_3)_2]_3$ and $[H_2BP(CF_3)_2]_4$ are among the products formed.[541] Although attempts have been made to prepare the adduct $H_3B.P(CF_3)_3$, no evidence for its existence could be found.[541] Other fluorophosphine boranes which have received study include $H_3B.P(t\text{-}Bu)_{3-n}F_n$[542], $H_3B.PPhF_2$[543], $H_3B.P(NMe_2)_{3-n}F_n$[370, 442], $H_3B.PF_2PH_2$[544], $H_3B.PF_2P(CF_3)_2$[544], $H_3B.P(OR)_{3-n}F_n$[370, 545–6], $H_3B.P(OCH_2CF_3)F_2$[545], and $H_3B.P(SMe)_{3-n}F_n$.[501] Towards BH_3, the established order of basicity is $PMeF_2 > P(NMe_2)F_2 > P(OMe)F_2 > P(SMe)F_2 \geqslant P(SMe)_2F$, which, except for the case of $PMeF_2$, parallels the order of the values of the $^1J_{PB}$ coupling constant.[501] The substitution of phosphinic fluorine by other halogens is associated with a progressive reduction in the basicity of the phosphine towards BH_3 with increasing atomic weight of the halogen[547], and likewise a progressive decrease in the value of the said coupling constant.[442] An attempt has been made to explain the basicity trend in terms of ligand-ligand repulsion between the ligands of the phosphine and borane moieties *inter alia*.[533] Borane(3) adducts of phosphines substituted by other halogens to have been investigated include $H_3B.PMe_2Cl$[548], $H_3B.P(t\text{-}Bu)_{3-n}Cl_n$[479, 542], $H_3B.P(NR_2)_{3-n}Cl_n$[549], $H_3B.P(OR)_{3-n}Cl_n$[549–50], $H_3B.PF_2Cl$[442, 547], $H_3B.PF_2Br$[442, 547] and $H_3B.PF_2I$.[547]

One borane(3) adduct of a fluoroarsine has been studied, i.e. $H_3B.As(NMe_2)F_2$.[551]

Here the boron is definitely attached to the arsenic and not the nitrogen, which is not true of the BF_3 adduct of the same base. The compound decomposes above -45°C.

ADDUCTS WITH COMPOUNDS OF GROUP-VI AND GROUP-VII ELEMENTS

Although no simple borane(3) adducts of free elements have ever proved isolable, BH_3O and BH_3O_2 have nevertheless been proposed as short-lived intermediates in the gas phase to explain features of the controlled reaction between diborane(6) and oxygen.[552-3] It seems reasonably certain that BH_3O is also a primary intermediate in the reaction of atomic oxygen with either B_2H_6 or B_4H_{10}[554],

$$O + B_2H_6 \rightarrow BH_3O + BH_3$$

$$O + B_4H_{10} \rightarrow BH_3O + B_3H_7$$

and there are reasons for believing that BH_3O_2 is probably present in B_2H_6 flames.[13]

The ionic species $[H_3BOH]^-$ is an intermediate in the acid hydrolysis of the BH_4^- ion. It has been identified by n.m.r. spectroscopy and its rate of disappearance at 20°C has been measured.[555] At lower temperatures (-78°C) the adduct $H_3B.OH_2$ is also formed as a very unstable intermediate that decomposes at a measurable rate by self-hydrolysis (hydrogen elimination)[555], and this compound has also been proposed as an intermediate in the hydrolysis of B_2H_6.[556] However, at low temperatures it can apparently change to a dimeric form of formula $[BH_2(OH_2)_2]^+[BH_4]^-$, since the cation $[BH_2(OH_2)_2]^+$ has been traced as an intermediate in its formation and disappearance.[555]

With alcohols at low temperatures similar adducts of type $H_3B.OHR$ are probably initially formed as intermediates, but only the dimeric forms have so far been identified from the B_2H_6 reaction.[557] It is in any case to be expected that the monomers would be subject to H_2-elimination by alcoholysis. But no comparable reaction can occur with ethers, whereupon the possibility arises that adducts of the type $H_3B.OR_2$ can be isolated, at least in solution. The oxygen-boron coordinate bond is however generally so much weaker than the nitrogen-boron bond in amine boranes, that positive identification of the ether adduct is difficult and has been accomplished with only a limited number of ethers. Clearly the energy liberated by coordination is here sufficiently low to become rather finely balanced with the energy absorbed in dissociating B_2H_6 into $2BH_3$. Diborane(6) generally has a very appreciable solubility in ethers, but in any given case at ordinary temperatures it is difficult to know just how much is present in the solution as BH_3 etherate and how much as dissolved B_2H_6 without dissociation.

No ether adducts are isolable at ordinary temperatures. Nevertheless, the evidence for the existence of loose BH_3 adducts with ethers at low temperatures is well documented. Thus $H_3B.OMe_2$ can be isolated at -80°C[190, 210], in spite of its very high dissociation pressure (Table VI) and complete dissociation in the gas phase. The n.m.r. evidence for its existence in solution is moreover quite convincing[558], and only slightly less so for the existence of $H_3B.OEt_2$[558-9]—which even at temperatures as low as -80°C is apparently undergoing fast equilibration. Further circumstantial evidence that the complex is indeed $H_3B.OEt_2$, is that the internal chemical shift of the alkyl protons is the same within the limits of measurement as for the more stable adduct $Me_3B.OEt_2$.[560] Phase studies give a weak confirmation of the existence of $H_3B.OEt_2$[210] without being really conclusive on their own because of the small variation in melting temperature over a wide concentration range. Tetrahydrofuran, being more basic than dialkyl ethers towards BH_3, dissolves a greater quantity of B_2H_6 and gives the adduct $H_3B.OC_4H_8$ (Table VI), which can be isolated below its melting point of -34°C.[561, 210] The established order of adduct stability is $C_4H_8O > Me_2O > Et_2O$.[562] Again dissociation is complete in the vapour phase at room temperature.[211] Solutions of B_2H_6 in tetrahydrofuran are in fact much used as a convenient effective source of BH_3 for many types of reactions. Such solutions are safe to store provided they are not sealed. The single case of an explosion which has been reported[563-4] occurred on prolonged storage of a sealed bottle, and appears to have been a pressure explosion caused by the slow release of hydrogen, either from reaction with traces of moisture within the bottle[565] or with $NaBH_4$ occasionally added as a stabilizer.[566] Dimethyl sulphide

Me_2S has been recommended as a satisfactory stabilizer.[567] The fully fluorinated ethers $(C_2F_5)_2O$ and cyclo-C_4F_8O form no adducts with BH_3.[210]

Apart from adducts formed by salts of carboxylic acids[568], which presumably contain anions of the type $[RCOO.BH_3]^-$, other types of oxygen compounds with carbonyl groups do not produce BH_3 adducts, except possibly as intermediates. To a large extent this may be because, apart from ethers, most oxygen compounds undergo reduction. Consequently the formaldehyde complex $H_2CO.BH_3$ is unknown, but it has been given a theoretical treatment.[420] Aminoacid esters $ROCOCH_2NH_2$ give borane(3) adducts, but here the boron is linked to the nitrogen and not to the oxygen.[569]

With hydrogen sulphide H_2S thiohydrolysis of BH_3 does not occur, but there is no evidence of adduct formation, even at temperatures as low as −78°C.[212] However, the thiolotrihydroborate ion $[H_3BSH]^-$ is produced from the interaction of B_2H_6 and lithium hydrogen sulphide below 0°C[570], and this is capable of adding on more BH_3 to give a bis adduct[571]

$$[H_3BSH]^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-78^\circ C} [HS(BH_3)_2]^-$$

The unstable ion $[HS(BH_3)_2]^-$ is also produced by the reaction of B_2H_6 with other base analogues that give rise to the SH^- ion in liquid H_2S.[572–4] Replacing the hydrogen on the sulphur by alkyl groups increases the donor strength of the sulphur, so that the bare existence of $H_3B.SHMe$[212] is demonstrable, while $H_3B.SMe_2$[192, 212] (Table VI) can be isolated below its melting point of −38°C. There is some chemical resemblance between the BH_3 adducts of thiols and of (primary and secondary) amines respectively. Thus $H_3B.SHMe$ readily loses H_2 to give a white ether-insoluble polymer of formula $(H_2BSMe)_x$, which on heating *in vacuo* undergoes partial depolymerization to volatile oligomers, at least temporarily.[212]

Under non-standard but specified conditions the enthalpy of the reaction

$$Me_2S + \tfrac{1}{2}B_2H_6 \rightarrow H_3B.SMe_2$$

is $-6{\cdot}1$ kcal mol^{-1}.[211] In the divalent state, sulphur is thus a stronger donor towards BH_3 than is oxygen, and the adducts of organic sulphides are everywhere considerably more stable than those of the corresponding oxygen compounds, a fact which is reflected in the greater solubility of diborane(6) in sulphides than in ethers.[575] There is thus a parallel with Group V, in which phosphorus is a stronger donor towards BH_3 than is nitrogen (p. 26). Even so, the strengths of the bonds formed by sulphur do not attain to those formed by either phosphorus or nitrogen.

The compound $H_3B.SMe_2$ is more stable than a solution of B_2H_6 in tetrahydrofuran, and keeps indefinitely on refrigeration, whereas C_4H_8O tends slowly to become cleaved by B_2H_6; also the former is very much more concentrated in BH_3. It has been recommended as a borane(3) carrier, as a reducing agent and a hydroborating agent with certain advantages over a solution of diborane(6) in tetrahydrofuran.[197, 576–8] It reduces aliphatic carboxylic acids smoothly and rapidly, but aromatic carboxylic acids only slowly unless excess trimethyl borate is added.[579]

The selenium analogue $H_3B.SeMe_2$ (Table VI) is similar,[192] but it is less stable and is completely dissociated in the gas phase.

Ions of the formula SR^- give complex ions of the type $[RS(BH_3)]^-$.[580] Thiophane borane $H_3B.SC_4H_8$ (Table VI) has also been studied.[211] It is not quite completely dissociated in the gas phase and has a dissociation pressure of only 4·64 Torr at 19·5°C, a mere fraction of that of $H_3B.OC_4H_8$. The thiocyanate ion gives the adduct $[H_3B.SCN]^-$, in which the boron may be linked to the sulphur rather than the nitrogen: at least, the ^{11}B n.m.r. spectrum is consistent with that structure.[291] Borane(3) also gives an adduct with ions of the type $[R_2CNS]^-$ [298], but it has not been established whether the boron preferentially links to the sulphur or the nitrogen. In adducts of formula $MeSNR_2.BH_3$ the boron is in all probability linked to the sulphur, since rearrangement to $MeSBH_2.NHR_2$ readily occurs and, on heating, $MeSBHNR_2$ is formed with the loss of hydrogen.[187] It is also believed that the sulphur atom is the donor in $H_3B.S(NMe_2)_2$.[213] Simple BH_3 adducts are formed neither by dimethyl sulphoxide Me_2SO[581] nor by sulphones $RR'SO_2$.[568]

No adducts are known in which borane(3) is directly linked to a halogen, except in the solitary case of the ionic species formed with the fluoride ion, $[H_3BF]^-$ [291],

$$KF+\tfrac{1}{2}B_2H_6 \xrightarrow[(CH_2OH)_2]{} K[BH_3F]$$

The ion $[H_3BF]^-$ has been the subject of theoretical treatment.[193, 185]

THE IONS BH_3^+ AND BH_3^-

The charged species BH_3^+ is known only in the mass spectrograph. It was first detected in electron-impact work with diborane(6), but in very low intensity[76], as was BD_3^+.[81] Later BH_3^+ was observed in the mass spectra of higher boranes, e.g. hexaborane(10)[80]; more recently it has been used as a means of identifying neutral BH_3 by electron impact.[83, 121, 11] Its appearance potentials from BH_3, B_2H_6, and BH_3CO have been determined as $12{\cdot}32 \pm 0{\cdot}10$[18], $14{\cdot}88 \pm 0{\cdot}05$[18] and $13{\cdot}70 \pm 0{\cdot}20$ eV[23] respectively.

The structure of BH_3^+ is doubtless planar[131], although experimental evidence is lacking. One B—H bond would be expected to be longer than the other two.

A derivative of BH_3^+ is the species BMe_3^+, which has been detected by ion cyclotron resonance spectroscopy.[115] Even as an isolated gaseous species its stability is limited by the fact that the energy of dissociation to $BMe_2^+ + CH_3$ is low ($7{\cdot}8 \pm 1$ kcal mol^{-1}).

The species BH_3^- has appeared in the negative-ion mass spectra of diborane(6) and other boranes[116, 90], and apparently can also be detected when diborane is bombarded by krypton ions.[582] Electron-spin-resonance studies have shown that BH_3^- is likewise present in γ-irradiated tetrahydroborates at 77 K.[583,584]

There is some doubt whether BH_3^- should be planar or pyramidal in its structure[131], and again experimental evidence is lacking. Because it is isoelectronic with CH_3, does not necessarily mean that it is also planar. *Ab initio* calculations indicate that it is pyramidal[585], but likely to depend on the environment.[586] A planar structure is however consistent with spin valence theory.[93] The B^- valence-state energy in BH_3^- has been calculated.[91]

The adduct species $Me_3N.BH_3^-$ has been detected by e.s.r. studies in the γ-irradiation of $Me_3N.BH_3$ at 77 K.[587] The species has resemblance to a perturbed BH_3^- radical ion according to theoretical calculations.

Substituted radical ions derived from BH_3^- are also known. Some triarylboranes of formula BAr_3 are cleaved by alkali metals, while others are not.[588] E.s.r. experiments have shown that, where this happens, the radical ion BAr_3^- is first formed, and, indeed, coloured salts of type $Na^+[BPh_3^-]$ have long been known.[589–90] The radical anion BPh_3^- is stable for a matter of weeks, but, on prolonged contact with alkali metal, biphenyl is slowly produced:[588]

$$BPh_3 + M \rightarrow M^+ + BPh_3^-$$

$$BPh_3^- + M \rightarrow PhPh + \text{products}$$

BORANE(4), BH_4, THE ION BH_4^+ AND THE TETRAHYDROBORATE(1−) ANION, BH_4^-

The species BH_4 has been proposed as occurring in the asymmetric decomposition of gaseous diborane(6)[83]

$$B_2H_6 \rightarrow BH_4 + BH_2$$

but it is now fairly certain that diborane decomposes preferentially in a different manner.[98] This is not to say that neutral BH_4 is intrinsically incapable of existence as a transient, non-isolable species, but experimental confirmation of its existence is lacking. The electron affinity of BH_4 has however been predicted by extrapolation from isoelectronic species as 33 kcal mol^{-1}.[34]

Since the free ion BH_4^+ has only 6 bonding electrons, it would predictably either not exist, or have at most a precarious existence. However, a claim to have observed it in the mass spectrum of tetraborane(10) has been made[591, 587], though this is not confirmed by another study.[592] Since BH_4^+, if it exists, bears a relationship to BH_3 like that which CH_5^+ bears to CH_4, its structure (in parallel with a theoretical investigation of the structure of CH_5^+ [593]) would be expected to contain one 3-centre HBH bond plus two 2-centre B—H bonds. It can moreover be predicted that the barrier to internal rotation of the pair of H atoms belonging to the 3-centre bond about the two-fold axis of symmetry of the normal BH_2 group would be larger than for the corresponding rotation in CH_5^+, where it is predictably low because of the staggered repulsion effects arising from the three-fold symmetry of the residual CH_3 group. And just as CH_5^+ rather readily breaks down into $CH_3^+ + H_2$, while apparently $B_2H_7^+$ readily gives $B_2H_5^+ + H_2$[594], the decomposition products of BH_4^+ can with considerable confidence be predicted to be $BH_2^+ + H_2$.

The negative ion BH_4^- is however a species of greater stability. In the gas phase, not only does it appear in high abundance in the negative-ion mass spectra of diborane(6) and other boranes[116, 90], but it has also been identified among the products of Kr^+ positive-ion impact with diborane.[582] Ion cyclotron resonance spectroscopy has shown that it undergoes gas-phase reactions, and the process

$$BH_4^- + B_2H_6 \rightarrow B_2H_7^- + BH_3$$

has been particularly well studied.[595]

The ionic species BH_4^- is sufficiently stable to exist in aqueous solution as the tetrahydroborate(1–) anion, which constitutes one of the well-defined boron-containing anions. It gives rise to a large number of stable crystalline salts, the tetrahydroborates (formerly called borohydrides), such as $NaBH_4$, $Mg(BH_4)_2$, and NMe_4BH_4 (for further details, see the section on tetrahydroborates, p. 354). The anion is capable of undergoing deuterium exchange with anhydrous D_2SO_4 or DF.[596]

The BH_4^- ion is isoelectronic with CH_4 and NH_4^+, and is tetrahedral in shape. It has been the subject of treatment by various theoretical approaches, including an optimized minimum basis wavefunction set[597], spin valence theory[93], an iterative extended Hückel method[598], approximate natural orbitals[599], and a floating spherical Gaussian orbital model.[113, 600] The B^- valence-state energy in BH_4^- has been estimated.[91]

The hydrogen atoms are bound less tightly in BH_4^- than in CH_4, The vibrational frequencies of BH_4^- and BD_4^- in liquid ammonia have been measured.[601–2] The symmetrical 'breathing' frequency $\tilde{\nu} = 2264$ cm^{-1} for BH_4^-, while the derived B—H stretching force constant is 3·04 mdyne Å^{-1} [603] (the corresponding figures for CH_4 are 2914 cm^{-1} and 5·04 mdyne Å^{-1}, respectively). The B—H bond length in free BH_4^- is presumably close to that found for it in its salts, namely *c.* 1·255 Å[604] (1·092 Å for C—H in CH_4). The enthalpy of formation of the ion BH_4^- in the gaseous state at 25°C has been estimated from thermochemical and crystal data as -23 ± 5 kcal mol^{-1}.[605] This value can be combined with other thermochemical data[29, 606] and an extrapolated value for the electron affinity of the boron atom (0·33 eV[607]) to give the value *c.* 89·6 kcal mol^{-1} for the mean B—H bond energy in BH_4^-, which is some 10% lower than the mean C—H bond energy in CH_4 (99·4 kcal mol^{-1}). The entropy of the gaseous BH_4^- ion at various temperatures has been calculated.[605, 608] For the aqueous BH_4^- anion, the enthalpy of formation at 25°C as obtained from thermochemical data is 11·51 kcal mol^{-1}.[29]

BORANE(5), BH_5, AND THE ION BH_5^+

The observation in the mass spectrometer of the ion CH_5^+, not only as a secondary ion[609–11], but also as a primary ion[612], and also the determination of the surprisingly large proton affinity of CH_4[613], raises the question of whether the isoelectronic species BH_5 can have transitory existence in the unimolecular region. As yet there is no experimental evidence to support or refute this proposition, but if BH_5 is capable of existence the question of its structure, whether that of an ion pair $H^+[BH_4^-]$ or something different, would be an interesting one. Theoretical considerations have not led to a unique structure for CH_5^+.[614–21] Different theoretical treatments of BH_5 have also given different molecular symmetries and stabilities, but the consensus of opinion is that the molecule is just stable with respect to $BH_3 + H_2$ ($\leqslant 10$ kcal mol^{-1}).[596, 622–4]

It would seem that BH_5 can also exist as a short-lived intermediate in aqueous solution, since hydrolysis data for tetrahydroborates over a wide pH range are consistent with the rate relationship[625–6]

$$-\mathrm{d}[BH_4^-]/\mathrm{d}t = k_1[H^+][BH_4^-] + k_2[BH_4^-]$$

and this is also compatible with the results of deuterium-exchange studies.[596, 626] Even earlier, the free acid $H[BH_4]$ had been proposed as an unstable intermediate in the reaction of $Mg(BH_4)_2$ with hydrochloric acid.[627] Clearly such a species, if it exists, will not be a conjugate protonated acid through lack of a lone pair of electrons. In non-aqueous media such as one of the anhydrous oxyacids H_3PO_4[628], H_2PO_3F[629], H_2SO_4 or HSO_3Cl[630], the hypothesized free acid breaks down immediately

$$2H[BH_4] \rightarrow B_2H_6 + 2H_2$$

at the temperatures conveniently employed in the production of diborane(6) from metal tetrahydroborates. Studies of these and similar reactions at really low temperatures have not been attempted.

The mass spectrum of $B_{10}H_{16}$[631] contains a strong line of mass number 16, which, if it is not due to impurity, must be ascribed to the positive ion BH_5^+, as also indicated in the monoisotopic mass spectrum obtained from a computerized least-squares treatment of the above data.[587] It has also been observed, though much less strongly, in the mass spectrum of B_4H_{10}.[591, 587]

THE IONS BH_6^+, BH_7^+ AND BH_8^+

The line due to mass number 17 has been observed rather strongly in the mass spectrum of $B_{10}H_{16}$ and that due to mass number 19 weakly.[631] A least-squares treatment of the data has indicated that the positive ions BH_6^+, BH_7^+ and BH_8^+ are all present.[587] Further experimental confirmation of their existence is as yet lacking. If they exist, this is an indication that the boron atom is capable of simultaneously participating in up to four 3-centre BH_2 bonds. Such structures would be expected to be very unstable.

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SECTION B2

DIBORANES AND THEIR DERIVATIVES

BY L. H. LONG

INTRODUCTION

Of the known neutral diborane species, only one, namely diborane(6) B_2H_6, is isolable at ordinary temperatures. Its chemistry thus constitutes the greater part of the present section, for it is also one of the most important compounds of boron, and one of exceptional interest for theoretical as well as practical reasons. Apart from this, certain bis adducts and substituted derivatives of diborane(4) can be isolated.

However, other diborane species have been recognized, both neutral and charged, and comprise molecules, radicals, ions and radical ions. Most of these have been produced by the fragmentation of diborane(6), but a number have also been observed during the fragmentation of higher boranes. Most of the charged species have been detected solely by mass spectrometry. Of the singly charged diborane ions, no true cations are known and only $B_2H_7^-$ has been observed as a true anion forming isolable salts and existing in solution. Ions with more than one positive charge have been detected in the mass spectrometer, but their intensity is very low and with one or two exceptions they do not require individual mention. The total abundance ratio of doubly to singly charged positive ions is only 0·0002 for B_2H_6 subjected to electron impact at 70 eV.[1]

To distinguish the conceivable structures of the diborane and higher borane species, use is made of the *styx*[2–3] and extended *styx*[4] topological notation, wherein *s* is the number of BHB bridge bonds, *t* the number of three-centre bonds, *y* the number of B—B single bonds, *x* the number of extra terminal hydrogen atoms on B—H (e.g. as BH_2 groups) and *v* is the number of vacant boron *p* orbitals. A computer program for listing the possibilities has been devised.[5]

DIBORANE(1), B_2H, AND THE IONS B_2H^+ AND B_2H^-

The radical B_2H is not known experimentally, but its electron affinity has been predicted.[6]

The positive ion B_2H^+ is known as a metastable ion from the mass spectra of diborane(6)[7–11] and other boranes[12–13], as is B_2D^+.[14–15]

The negative ion B_2H^- has been observed in the negative-ion mass spectra of diborane(6) and pentaborane(9).[16]

DIBORANE(2), B_2H_2, AND THE IONS $B_2H_2^+$ AND $B_2H_2^-$

Although B_2H_2 has not been directly observed, it doubtless has transitory existence in the unimolecular decomposition of octaborane(12) to hexaborane(10).[17–18]

$$B_8H_{12} \rightarrow B_6H_{10} + B_2H_2$$

What is observed, however, is a yellow non-volatile polymer of formula B_nH_n. From this it is apparent that B_2H_2 polymerizes rapidly, which would be consistent with its highly unsaturated nature. The skeleton of octaborane(12)[19] is closely related to that of hexaborane(10), having two adjacent and interlinked boron atoms appended to the base of the pentagonal pyramid of the latter compound. It is doubtless these two boron atoms which are shed initially in the form of B_2H_2. The ground state is predicted to be a triplet, namely $^3\Sigma_g^-$.[20] No monomeric adducts of B_2H_2 have been reported, which is not surprising in view of the disinclination of boron to form stable multiple bonds. Even for such polymeric forms as have been claimed, it is at least questionable whether these are not more correctly regarded as adducts of B_4H_4. Thus the reported $(Me_2S.B_2H_2)_{2n}$, produced in the reaction of dimethyl sulphide with pentaborane(9)[21]

$$3Me_2S + B_5H_9 \xrightarrow{250°C} H_2 + Me_2S.BH_3 + \frac{1}{n}(Me_2S.B_2H_2)_{2n}$$

is probably more correctly written as $(B_4H_4.2SMe_2)_n$.

The positive ion $B_2H_2^+$ is observed in the mass spectra of diborane(6)[7–10] and higher boranes[12–13], as is $B_2D_2^+$.[14–15] By means of ion cyclotron resonance spectrometry, it has been shown that $B_2H_2^+$ reacts in the following way with methanol in the gas phase[22]

$$B_2H_2^+ + CH_3OH \rightarrow B_2H_2OH^+ + CH_3$$

The doubly charged ions $B_2H_2^{2+}$ [9] and $B_2D_2^{2+}$ [12] have been identified.

The negative ion $B_2H_2^-$ is one of the species that appear in the negative-ion mass spectra of boranes.[23, 16]

THE IONS $B_2H_3^+$ AND $B_2H_3^-$

Although neutral B_2H_3 is not known, the positive ions $B_2H_3^+$ and $B_2D_3^+$ have been identified in the mass spectra of boranes.[7–10, 12–15] The bis-carbonyl adduct ion $B_2H_3(CO)_2^+$ has also been identified in the mass spectrum of $B_2H_4(CO)_2$.[24]

The negative ion $B_2H_3^-$ occurs in the negative-ion mass spectrum of boranes[23, 16] and has been tentatively identified as one of the products of bombarding diborane(6) with krypton ions.[25] It has been treated theoretically[1006] and assigned the structure $HB{=}BH_2^-$.

DIBORANE(4), B_2H_4, AND THE IONS $B_2H_4^+$ AND $B_2H_4^-$

Both adducts and substituted derivatives of B_2H_4 are known. However, all attempts to isolate monomeric B_2H_4 have failed, and all the available evidence suggests that it is too electron-deficient to exist as a monomer, except possibly as a transitory intermediate.[24] Even a suggestion[26] that B_2H_4 plays a role in the formation of higher boranes from pyrolyzing diborane(6) has been withdrawn.[27] On the extended *styx* notation, the $0012(v=2)$ structure of B_2H_4 is theoretically the most stable.[4] According to an approximate *ab initio* partial retention of diatomic differential overlap (PRDDO) treatment, this is about 100 kcal mol^{-1} more stable than the disallowed B—B π-bonded $2010(v=0)$ structure, and for the 0012 structure the staggered conformation is a calculated 13·1 kcal mol^{-1} more stable that the eclipsed.[4] Other methods of calculation provide results that are rather similar.[20, 28–9, 1006] Decomposition of B_2H_4 into $BH + BH_3$ requires considerably less energy than decomposition into $2BH_2$.[28] The bond lengths predicted by a non-empirical MO technique are 1·683 and 1·202 Å for the B—B and B—H bonds respectively, while the angle HBH is 116·2°.[29] The vacant orbital on each of the boron atoms would give rise to the expectation that the molecule, if formed, would be liable to immediate polymerization, and there is experimental evidence to support this. Thus the extraction of two BH_3 groups from B_4H_{10} by treatment with trialkylboranes leads not to the monomer, but to the polymeric species $(B_2H_4)_n$.[30–3]

$$B_4H_{10} + 4BEt_3 \xrightarrow{3°-10°C} \frac{1}{n}(B_2H_4)_n + 3B_2H_2Et_4$$

In practice, 6 parts of BEt_3 to 1 part of B_4H_{10} are used, and the reaction requires several days to proceed to completion. The $(B_2H_4)_n$ produced contains 50% of the boron from the B_4H_{10}. It is a solid that loses hydrogen above 120°C. At present there is no evidence that it can be produced by direct condensation of a presumed monomer. The infra-red spectrum indicates that the polymer contains both B—H bonds and BHB bridges, but no BH_2 groups, while the ^{11}B n.m.r. spectrum shows a single broad band.[33] Other attempts to prepare B_2H_4 (e.g. by the reduction of B_2Cl_4 with $LiAlH_4$[30]) have led to different products.

The first definite adduct of B_2H_4 to be isolated and characterized was the bis-triphenylphosphine adduct $B_2H_4.2PPh_3$, formed as a relatively stable solid by the cleavage of trimethylamine triborane(7) or dimethylaminodifluorophosphine triborane(7) with excess triphenylphosphine[34–5]

$$Me_3N.B_3H_7 + 3PPh_3 \xrightarrow[50°C]{C_6H_6} B_2H_4.2PPh_3 + H_3B.PPh_3 + NMe_3$$

The central $B_2H_4P_2$ section of the molecule has an ethane-like structure with the anti conformation in the solid phase and a B—B bond length of 1·76Å[35], i.e. barely shorter than that in B_2H_6 (p. 57). Coordination nevertheless satisfies the electron-deficient nature of the parent borane and stabilizes the boron-boron bond, which becomes resistant to acid hydrolysis, though at 100°C it can be slowly cleaved by alcoholic potassium hydroxide.[34] Several other bis-phosphine adducts have since been prepared, including $B_2H_4.2PF_3$[36–7], which is much less stable and decomposes rapidly at room temperature by bimolecular steps, giving hexaborane(12) as a major product. In the gas phase the B—B bond length is 1·800 ± 0·036 Å.[38] More stable is $B_2H_4.2PHF_2$, which melts at 43°C with only slight decomposition.[39] The order of stability thus recalls that for $H_3B.PF_3$ and $H_3B.PHF_2$. There is, however a decreasing stability in the series $B_2H_4.2PF_3 > B_2H_4.2PF_2Cl > B_2H_4.2PF_2Br$.[40] Also characterized is $B_2H_4.2PF_2(NMe_2)$.[39,41] All these fluorophosphine derivatives are prepared from the dimethyl ether adduct of triborane(7). Diborane(6) readily converts such adducts into B_4H_{10}[37,39]

$$B_2H_4.2PF_2X + B_2H_6 \rightarrow B_4H_{10} + 2PF_2X \ [X = F, H, NMe_2]$$

Very little information is available concerning B_2H_4 adducts with nitrogenous bases. One has been reported to be formed by the interaction of pyridine and tetraborane(10) at 0°C[42], but the reputed formula $B_2H_4.NC_5H_5$ is unexpected and still awaits confirmation.

One of the more interesting adducts of diborane(4) is the bis-carbonyl 1,2-$B_2H_4(CO)_2$, first reported in 1974.[24] It is prepared in poor yield as one of the products of decomposition of B_3H_7CO held at 0°C for 2 h. Since the presence of carbon monoxide under pressure in no way assists the reaction, but rather reduces the yield, it is apparent that $B_2H_4(CO)_2$ is not formed by the replacement of a BH_3 group of B_3H_7CO by CO. Because of the similarity in volatility of $B_2H_4(CO)_2$ to unchanged B_3H_7CO and B_4H_{10} (a principal product of the reaction), a low-temperature fractionating column is needed to separate it. It melts in the range −110 to −100°C and can be sublimed at −110°C. The infra-red, ^{11}B n.m.r. and mass spectra have been recorded, while an X-ray structure determination with a single crystal has shown that with respect to the two boron atoms the molecule has a geometrical structure like a 1,2-disubstituted ethane, the two carbonyl 'substituents' taking up positions as far from each other as possible, thus giving the molecule a centre of inversion.[24] The molecular parameters are reproduced in Table I. These are broadly in accordance with expectation. The B—B distance is slightly longer than in B_2H_6 and the B—C distance somewhat shorter than in BH_3CO. It is to be

Table I.—Molecular Parameters of 1,2-$B_2H_4(CO)_2$ in the Crystalline Phase[(a)]

Internuclear distance	Value (Å)	Interbond angle	Value
r(B—B)	1·78 ± 0·01	∠B—B—C	102·3 ± 0·5°
r(B—C)	1·52 ± 0·01	∠B—C—O	177·5 ± 0·6°
r(C—O)	1·125 ± 0·007	∠B—B—H_1	115 ± 3°
r(B—H_1)	1·14 ± 0·06	∠B—B—H_2	117 ± 3°
r(B—H_2)	1·11 ± 0·06	∠C—B—H_1	108 ± 3°
		∠C—B—H_2	100 ± 3°
		∠H_1—B—H_2	112 ± 4°

[(a)] From X-ray structure analysis, Ref. 24.

presumed that the non-equivalence of the hydrogen atoms and the departure of the BCO angle from 180° are due to solid-phase distortions and would disappear in the gas phase. The molecule has been studied theoretically by a non-empirical MO technique, and the difference in energy between the eclipsed and staggered conformers calculated to be 74 kJ mol^{-1}.[29] Nothing has been reported concerning its reactions, except that it is *c.* 88% decomposed on being allowed to stand at 27°C for 15 min.[24] The principal products are CO, BH_3CO and small amounts of B_6H_{12}, plus a non-volatile solid and an unidentified liquid borane carbonyl of low volatility.

Although B_2H_4 is not isolable, many of its substituted derivatives are preparable. First to be reported was B_2Cl_4 by Stock[43–4], who decomposed boron trichlorides in the electric arc between zinc electrodes

$$2BCl_3+Zn \xrightarrow{\text{electric discharge}} B_2Cl_4+ZnCl_2$$

Except in the solid state, the molecule is non-planar.[45] It is highly reactive and will, for example, cleave the cyclopropane (but not cyclobutane) ring[46], add two BCl_2 groups across a C=C double bond[47] and additionally undergo fluorine-chlorine exchange with fluoro-olefins.[48] Other simple derivatives include $B_2(NMe_2)_4$[49–50], $B_2(OMe)_4$[51, 50], $B_2(SMe)_4$[52] and B_2F_4[53], prepared by such reactions as:

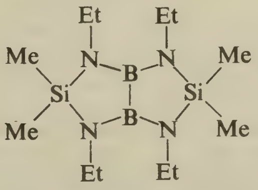
$$2(Me_2N)_2BCl+2K \xrightarrow[0°C]{} B_2(NMe_2)_4+2KCl$$

$$B_2(NMe_2)_4+4MeOH \xrightarrow[30°-50°C]{} B_2(OMe)_4+4NHMe_2$$

$$B_2(NMe_2)_4+4MeSH+4HCl \xrightarrow[25°C]{CH_2Cl_2} B_2(SMe)_4+4NH_2Me_2Cl$$

$$2(BO)_n+2nSF_4 \xrightarrow[-80°C]{} nB_2F_4+2nSOF_2$$

These derivatives show a moderate thermal stability, restricted by the comparative weakness of the B—B bond. Unlike B_2Cl_4, the B_2O_4 skeleton of $B_2(OMe)_4$ is planar, but in $B_2(NMe_2)_4$ the BN_2 groups are twisted out of the molecular plane.[54] The latter compound has been examined theoretically.[55–7] It undergoes photochemically induced reactions with CCl_4, $CHCl_3$ and CH_2Cl_2[58], and reduces vanadium(IV) to vanadium(III).[59] Titanium tetrabromide is also reduced, one of the products of reaction being 1,2-dibromo-1,2-bis(dimethylamino)diborane(4) $B_2(NMe_2)_2Br_2$.[60] Much more complicated derivatives of B_2H_4 have been prepared, such as the bicyclic compound[61]



It will be noticed that in the above derivatives all the atoms attached to the boron atoms possess lone pairs of electrons, and are thus through a measure of π bonding able to reduce the electron-deficient nature of the boron atoms. It is however not necessary for all four substituents to possess lone pairs, so that the compounds 1,2-dimethyl-1,2-bis(dimethylamino)diborane(4) $B_2Me_2(NMe_2)_2$[62] and 1,2-dichloro-1,2-dimethyldiborane(4) $B_2Me_2Cl_2$[63] have been reported, the latter arising from the interaction of $BMeCl_2$ with copper atoms. The mass spectra of $B_2Et_2(NMe_2)_2$ and related compounds have been published.[64] Even the tetrapropyl compound B_2Pr_4 has been claimed[65] as a liquid boiling at 56°–63°C at a pressure of 12 Torr, but this is an isolated example of a derivative in which none of the substituents possess lone electron pairs to provide for π bonding. There is no published report of any B_2H_4 derivative in which part of the hydrogen remains attached to boron, but reference has been made in a private communication[66] to the preparation of the unstable compound $B_2H(NMe_2)_3$ by the reduction of chlorotris(dimethylamino)diborane(4) with lithium hydride. Also the unknown molecule $B_2H_2(NH_2)_2$ has been studied theoretically.[57] Since derivatives of B_2H_4 are typical diboron compounds, the Section B14 should be referred to for further details.

The ionic species $B_2H_4^+$ and $B_2D_4^+$ are known in the mass spectrograph[7–10, 12–15], but have not otherwise been observed. By means of ion cyclotron resonance it has been shown that the ion reacts with methanol and dimethyl ether in the gas phase in the following manner[22]:

$$B_2H_4^+ + CH_3OH \rightarrow B_2H_2OH^+ + H_2 + CH_3^{\cdot}$$

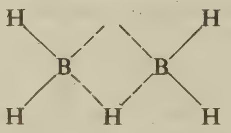
$$B_2H_4^+ + (CH_3)_2O \rightarrow B_2H_2OMe^+ + H_2 + CH_3^{\cdot}$$

The ion $B_2H_4^-$ occurs in the negative-ion mass spectra of boranes.[23, 16] The tetraphenyl derivative, the anion $B_2Ph_4^-$, has apparently been identified, from its electron spin resonance spectrum, as a product of the reaction of chlorodiphenylborane Ph_2BCl with sodium-potassium alloy.[67] The hyperfine structure indicates that the unpaired electron is interacting with both boron nuclei, i.e. that it is involved in the boron-boron bonding.

A theoretical study of the unknown $B_2H_4^{2-}$ ion shows that the eclipsed structure is much more stable than the staggered, which indeed is completely unstable with respect to $2BH_2^-$.[29] Its predicted structure is therefore like that of the isoelectronic ethylene molecule.

DIBORANE(5), B_2H_5, AND THE IONS $B_2H_5^+$ AND $B_2H_5^-$

Diborane(5), the diboranyl radical B_2H_5, must be regarded as the simplest borane species in which some form of hydrogen bridge bonding is to be expected. Although it does not occur in the low-temperature pyrolysis of diborane(6), it is considered to be a primary radical produced in the photolysis of this compound[68–9], where the available energy is much greater. At least, the kinetics of decomposition are most readily explained on this assumption. Confirmation of its existence has been demonstrated by the e.s.r. spectrum of β-B_2H_6 irradiated with γ-rays at 77 K.[70–1] The B_2D_5 radical was detected in a similar way. From the variation of the spectrum with the angle of rotation of a single crystal, it has been possible to show that the structure of B_2H_5, at least in a solid B_2H_6 matrix, is fundamentally similar to that of B_2H_6 itself with one bridge hydrogen atom missing.

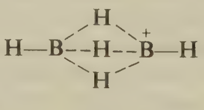


The remaining bridge hydrogen atom is equally shared between the two boron atoms, and the bond angle between the principal axes of the two boron atoms is c. 73°. There is also evidence that both of the H_2BB groupings deviate from strict planarity.[72] This structure harmonizes well with the results of theoretical studies.[71, 73]

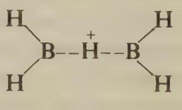
The positive ion $B_2H_5^+$ is known (as is $B_2D_5^+$) from the mass spectrum of diborane(6)[7–15], in which it occurs with high intensity. Its appearance potential has been measured as $11{\cdot}84 \pm 0{\cdot}1$ eV.[74] It is also produced in an ion-molecule reaction between CH_5^+ and B_2H_6[75]

$$B_2H_6 + CH_5^+ \rightarrow B_2H_5^+ + CH_4 + H_2$$

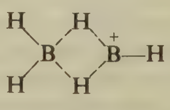
and is apparently the first decomposition product of $B_2H_7^+$.[76] There is evidence that $B_2H_5^+$ commences to break down with the liberation of hydrogen at about 490 K.[27] Three possible structures have been considered:



(a)



(b)



(c)

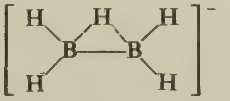
By an analogy with acetylene, the triply hydrogen-bridged structure (*a*) does not appear to be unreasonable[77], and it has found support from the most recent theoretical calculations based upon *ab initio* FSGO and CNDO/2 treatments[78], but other procedures lead to different results and favour the singly-bridged planar structure (*b*).[79] The reactions of the $B_2H_5^+$ ion with certain alcohols and ethers in the vapour phase have been investigated and found to follow the general path[22]

$$B_2H_5^+ + ORR' \rightarrow H_2BORR'^+ + BH_3 \quad [R = H, Me; R' = Me, Et, n\text{-}Pr]$$

The negative ion $B_2H_5^-$ has been encountered, not only in the negative-ion mass spectra of boranes[23,16], but among the products of positive-ion impact of diborane(6).[25] An indication that it is also formed in the gas-phase reaction

$$BH_4^- + B_2H_6 \rightarrow B_2H_5^- + BH_3 + H_2$$

has been provided by ion cyclotron resonance studies.[80] Its structure is unknown, but according to an *ab initio* study[1006] it is not analogous to that of borylmethane CH_3BH_2, with which it is isoelectronic, but symmetric with the bridging hydrogen atom in a plane perpendicular to that of the two BH_2 groups:



DIBORANE(6), B_2H_6

General

Diborane(6) B_2H_6 is the simplest borane that is isolable, although it was not in fact the first borane to be prepared and identified. It was discovered during the researches of 1912–13 by Alfred Stock[81], the pioneer in the field of boron hydrides. The hydride B_2H_6 may be regarded as the first member of the hydrogen-poorer borane series B_nH_{n+4} (as distinct from the hydrogen-richer series B_nH_{n+6}, typified by tetraborane(10) B_4H_{10}); but it is more useful to classify the isolable boranes into the principal divisions $(BH)_m(BH_3)_2$ and $(BH)_m(BH_3)_3$, into which, with some exceptions, the known members fit. According to the latter classification, B_2H_6 is the lightest member of the first series and has $m = 0$. It would therefore be expected to possess special properties, and this is borne out by observation.

For several decades after its discovery, diborane remained a relatively inaccessible compound. Only since the Second World War has the position changed with the discovery of numerous improved methods of preparation. The compound is now easily prepared in the laboratory and knowledge of its chemistry has been vastly extended, especially since the mid-1950s.

Owing to its unique and highly reactive nature, diborane(6) has an unusually varied chemistry and has become a valuable reagent, not only for use in the very important hydroboration procedure, but also in many other types of reactions. Indeed, it reacts in various respective ways with the majority of compounds, and so may rightly be regarded as one of the most reactive compounds known. In most cases chemical change sets in at or below room temperature, so that its reactions are generally to be associated with low activation energies.

With the discovery of the nature of the covalent bond, it became apparent that the molecular structure of B_2H_6 is incapable of being depicted by any ordinary valence-bond model. The number of available valence electrons is insufficient to provide a separate pair for each pair of bonded atoms, however these are arranged, so that the molecule is strongly electron deficient. This fact incontrovertibly contributes to the high reactivity of diborane and also helps to account for the low activation energies of reactions with which it is associated. Moreover, it is the simplest electron-deficient molecular species that is capable of isolation. Diborane(6) thus presented for a long time a unique challenge to chemists and has a fascination of its own. As summarized elsewhere[82], various special types of bonding (now only of historical interest) were proposed before the currently accepted hydrogen bridge-bond structure was settled experimentally in 1951[83] and subsequently confirmed by a satisfactory mathematical explanation of the observed vibrational frequencies of B_2H_6 and B_2D_6 on the basis of this model.[84] A bridge-bond structure had in fact been proposed speculatively as early as 1921[85], and the first modern attempts to understand the nature of the bridge bond stem from the year 1943.[86–8] Since that time diborane(6) has been the subject of much theoretical treatment.

Molecular Properties and Related Matters

MOLECULAR STRUCTURE AND CHARGE DISTRIBUTION

Diborane(6) possesses four equivalent terminal B—H bonds and two equivalent 3-centre BHB electron-pair bridge bonds. Thus, although the boron atoms are geometrically equivalent, there are two different types of hydrogen atoms, termed the terminal and bridge hydrogen atoms respectively. The molecule is shown diagrammatically in Fig. 1, in which the two bridge hydrogen atoms lie on an axis that is perpendicularly bisected by the plane of the other six atoms. There are three mutually perpendicular twofold axes of symmetry (point group D_{2h}). The dimensions are given in a recent detailed analysis and conflation[89] of electron-diffraction data[90] with the results of high-resolution infra-red spectroscopy.[91] Relevant information is listed in Table II, which also includes electron-diffraction results for deuterodiborane. Even in the absence of microwave data, it can be said that the parameters of diborane are now as accurately known as those for almost any other molecule of comparable size. X-ray diffraction studies have yielded bond lengths that are much shorter.[92–3] Differences in the mean amplitudes of vibration obtained from the various methods have received comment.[94–5] The arrangement of the four hydrogen atoms about either boron atom is far from being that of a regular tetrahedron, but may be regarded as a disphenoid with the edge joining the bridge hydrogen atoms slightly shortened, while the boron atom is off-centre and displaced away from this edge.

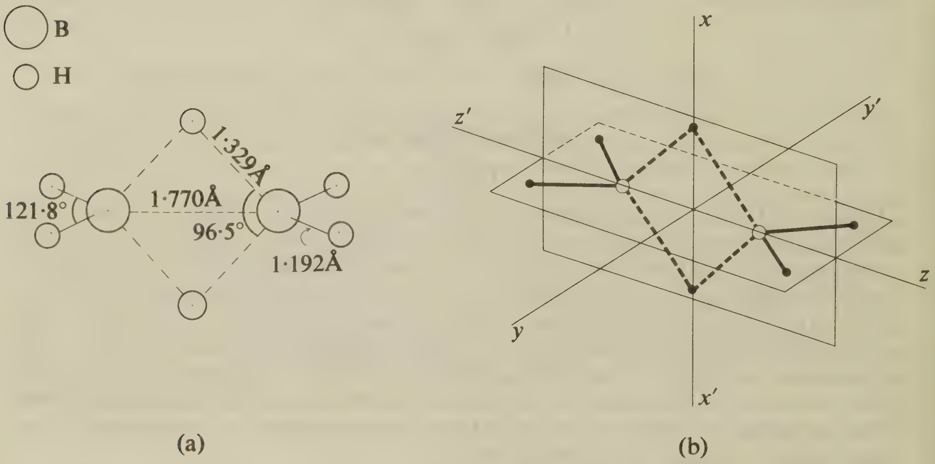


FIG. 1.—The structure of diborane: (*a*) with molecular parameters for the ground vibrational state from Ref. 89; (*b*) showing the three non-identical, mutually perpendicular twofold axes of symmetry, *xx′*, *yy′* and *zz′*

Although numerous attempts have been made during the last two decades to describe the bonding along theoretical lines, none of these can be said to provide a perfect picture of the electron distribution in diborane. Different approaches frequently give widely diverging results. For example, one LCAO molecular-orbital treatment on the

Table II.—Molecular Parameters of Diborane(6) and Deuterodiborane(6)

Borane	Parameter(a)	E.D.(b)	E.D.(corr.)(c)	I.R.(d)	Averaged(e)
B_2H_6	B—H_t (Å)	1·196$_0$	1·180	1·200$_5$	1·19$_2$ ± 0·01
	B—H_b (Å)	1·339$_3$	1·329	1·320$_4$	1·32$_9$ ± 0·005
	B—B (Å)	1·775$_0$	1·774	1·762$_8$	1·77$_0$ ± 0·005
	$\angle H_tBH_t$	120·2°	118·8°	121·0°	121·8° ± 3°
	$\angle H_bBH_b$	97·0°	96·2°	96·2°	96·5° ± 0·5°
B_2D_6	B—D_t (Å))	1·198$_0$	1·187		
	B—D_b (Å)	1·333$_5$	1·326		
	B—B (Å)	1·771$_2$	1·770		
	$\angle D_tBD_t$	122·4°	121·4°		
	$\angle D_bBD_b$	96·8°	96·2°		

(a) Subscripts *t* and *b* refer to terminal and bridge positions respectively.

(b) Experimental electron-diffraction values (Ref. 90). The distances are r_g values (average internuclear distances).

(c) The electron-diffraction values adjusted (Ref. 89) to absolute zero and for the effect of vibrational amplitude with the aid of moments of inertia derived from high-resolution infra-red spectroscopy. The distances listed refer to the ground vibrational state.

(d) Parameters calculated from high-resolution infra-red spectra (Ref. 91). The B—H distances are r_0 values and the B—B distance r_s.

(e) Average parameters (Ref. 89). The distances are r_z values, i.e. gas-phase average internuclear distances for the ground vibrational state.

basis of Gaussian functions[96] gives a model with two 3-centre banana bonds with practically no bond between the boron atoms (as implied by the overlap of electron populations), whereas boron-boron bonding is strongly implied by a calculation of the potential constants for diborane.[97] Not only the sizes but even the signs of the atomic charges are in doubt, and results from the former treatment[96] are almost the opposite of those from an alternative LCAO-MO calculation.[98] Theoretical treatments tend to exaggerate the charges, which are probably quite small, with the hydrogen atoms negatively charged, and the negative charge of the terminal atoms greater than that of the bridge atoms. The low values provided by an optimized minimum-basis-set SCF calculation[99], $-0{\cdot}032$ and $-0{\cdot}001$ respectively, would seem to be as reasonable as any. The geometry of the molecule is particularly well predicted by a recent *ab initio* calculation based on a floating spherical Gaussian orbital model[100], even though it gives the wrong sign for the bridge-bond dissociation energy. Other recent treatments make use of a semi-empirical method[101], an iterative extended Hückel method[102], equivalent orbitals[103], and an *ab initio* SCF approach.[104] Most modern approaches assume two open 3-centre BHB bonds, and studies such as one investigating the effect of varying effective nuclear charge on the bond angle and energy of the 3-centre bonds[105] are useful. Nevertheless, reasons have emerged for considering a 3-centre molecular-orbital function to be slightly inferior to a non-paired spatial orbital function in diborane.[106]

Difficulties in the theoretical approaches lie in the underlying assumptions. One such assumption, following a suggestion originally made in 1954[107], and adopted almost universally since[2], being based on earlier work on the carbon atom with four equally occupied orbitals[108], is that the boron atoms are in the sp^3-hybridized state. This is certainly a false assumption, and leads to too little *s* character in the bonds involving the terminal hydrogen atoms and too much in the bridge bonds, as well as to exaggerated atomic charges. In reality, the size of the angle between the two terminal bonds is far from that of the tetrahedral angle, but is very close to the 120° required by sp^2 hybridization. The third sp^2 bond is best regarded as replaced by two half-bonds[109], which are splayed out in a plane perpendicular to that of the terminal bonds to form the bridge. On this view the mixing with the vacant *p* orbital is essentially confined to this third sp^2 orbital: this approach has only occasionally been adopted.[110–11]

Table III.—Fundamental Vibrational Frequencies of Four Isotopic Species of Diborane(6)

Symmetry species	Fundamental(a)	Approximate description of vibrational mode	Vibrational frequency (cm^{-1})(b)			
			$^{11}B_2H_6$	$^{10}B_2H_6$	$^{11}B_2D_6$	$^{10}B_2D_6$
A_g	ν_1	BH_t stretch, sym. in-phase	2,530·2(c)	2,536·8(c)	1,865·9(c)	1,870*(d)
	ν_2	BH_b stretch, sym. in-phase	2,112·2(c)	2,112·2(c)	1,517·0(c)	1,514*(d)
	ν_3	H_tBH_t def., in-phase	{1,184(d) 1,317·6(c)	{1,186(d) 1,322·0(c)	{912*(d) 931·2(c)	928*(d)
	ν_4	B· · ·B stretch	790·0(c)	818·0(c)	710·5(c)	721(d)
A_u	ν_5	BH_2 twist, opp. direction	833·1(e)	833(e)	592(e)	592(e, f)
B_{1g}	ν_{11}	BH_t stretch, asym. out-of-phase	2,597(c)	2,600(c)	1,975(c)	1,990(d)
	ν_{12}	BH_2 rock, same direction	914(g)	930(h)	(725)(e)	(728)(e)
B_{1u}	ν_{13}	BH_b stretch, sym. out-of-phase	1,880(i)	1,887(f)	1,461(j)	1,491(i)
	ν_{14}	BH_2 wag, opp. direction	972·7(k)	977·3(l)	722(j)	728(f)
B_{2g}	ν_6	BH_b stretch, asym. out-of-phase	{1,755(d) 1,780(c)	{1,768(d) 1,800(c)	{1,287(d) 1,295(c)	1,285(d)
	ν_7	BH_2 wag, same direction	{c.850(e) 856 (s)(m)	c.850(e)	{(c.698)(e) (c.710)(i)	(c.698)(b)
B_{2u}	ν_8	BH_t stretch, asym. in-phase	2,608·85(n)	2,622·70(n)	1,994(j)	1,999(f)
	ν_9	BH_2 rock, opp. direction	934 (s)(i)	. . .	. . .	703 (s)(f)
	ν_{10}	B_2H_2 ring pucker	369·3(o)	368(f)	261·3(o)	262(f)
B_{3g}	ν_{15}	BH_2 twist, same direction	1,025(d)	1,030(d)	744(p)	748(d)
B_{3u}	ν_{16}	BH_t stretch, sym. out-of-phase	2,519·65(n)	2,525·02(n)	1,850(j)	1,857(f)
	ν_{17}	BH_b stretch, asym. in-phase	1,600·8(l)	1,606(f)	1,203(j)	1,205(f)
	ν_{18}	H_tBH_t def., out-of-phase	1,173·8(k)	1,181·7(l)	876·0(l)	881(f)

(a) The numbering is that adopted in Ref. 88.

(b) The values are selected from Refs. 91 and 113–22. Values marked with an asterisk (*) have been corrected for Fermi resonance. All values refer to the gas phase, except for those marked (s), which refer to the solid phase. Values in parentheses ( ) have not been directly observed, but have been calculated from values for isotopic molecules by means of the product rule.

(c) Ref. 122. (d) Ref. 115. (e) Ref. 118. (f) Ref. 114. (g) From combination $\nu_{10}+\nu_{12}$ at 1,283·1 cm^{-1} in Ref. 118. (h) From combination $\nu_{10}+\nu_{12}$ at 1,298 cm^{-1} in Ref. 114. (i) Ref. 119. (j) Ref. 113. (k) Ref. 120. (l) Ref. 117. (m) From combination $\nu_7+\nu_{17}$ at 2,443 cm^{-1} and ν_{17} at 1,587 cm^{-1} for the solid in Ref. 119. (n) Ref. 91. (o) Ref. 121. (p) From first overtone at 1,488 cm^{-1} in Ref. 115.

VIBRATIONAL SPECTRA

One of the earlier investigators[112], following theoretical predictions of possible vibrational modes[7] of the structural model now unequivocally accepted, showed that 15 of the 18 fundamentals could be directly observed in either the infra-red or Raman spectra, and a number in both. Several spectroscopic studies of $^{11}B_2H_6$, $^{10}B_2H_6$, $^{11}B_2D_6$ and $^{10}B_2D_6$ with partially successful assignment attempts followed.[113–17] In 1964, two of the missing fundamentals were located from observations of Coriolis perturbations, which enabled a more definitive set of spectroscopic assignments based on earlier infra-red and Raman work to be made, as well as a prediction of the position of the third missing fundamental.[118] The last, however, has since been observed in the infra-red spectrum of solid diborane(6) in a polycrystalline film[119], so that experimental values are now available for all the fundamental frequencies of $^{11}B_2H_6$. Several infra-red bands have been studied by high-resolution spectroscopy.[120, 91, 121] Table III presents a judicial selection of experimental values for the fundamental frequencies of four isotopic species of diborane(6). As is seen, the most recent and accurate Raman study[122] proposes a reassignment of the BH_2 deformation fundamental ν_3 in $^{11}B_2H_6$ and $^{10}B_2H_6$ from 1,184 and 1,186 cm^{-1} respectively to the revised values 1,317·6 and 1,322·0 cm^{-1}. The infra-red evidence accords better with the older values, however, and the new assignments must be regarded as questionable until confirmation is forthcoming, especially as Raman frequencies appropriate for the BH_2 deformation vibration in methyldiborane(6) and 1,1-dimethyldiborane(6) lie at 1,164[123] and 1,163 cm^{-1} [124] respectively. For the isotopic species $^{11}B^{10}BH_6$ and $^{11}B^{10}BD_6$ a few lines have been identified in the Raman[122] and infra-red[117], but vibrations that might have become active on account of the lower symmetry arising from the non-identical boron atoms did not appear in the infra-red spectrum of $^{11}B^{10}BH_6$. Spectra of the partially deuterated species B_2H_5D and B_2HD_5 have been reported[125] and used to calculate the vibrational frequencies of 12 other partially deuterated forms of diborane(6).[126]

From high-resolution infra-red spectra[91] the moments of inertia of $^{11}B_2H_6$ and $^{10}B_2H_6$ have been calculated with high precision (see Table IV), as have the molecular parameters (Table II).

Table IV.—Principal Moments of Inertia of $^{10}B_2H_6$ and $^{11}B_2H_6$[(a)]

Borane	I_a (amu Å^2)	I_b (amu Å^2)	I_c (amu Å^2)
$^{10}B_2H_6$	6·3481 ± 0·0013	26·2500 ± 0·0032	28·6999 ± 0·0032
$^{11}B_2H_6$	6·3477 ± 0·00061	27·7964 ± 0·0032	30·2496 ± 0·0030

[(a)] Derived from the high-resolution infra-red work of Ref. 91.

ULTRAVIOLET SPECTRUM

Early studies of the ultraviolet absorption of diborane(6) revealed a weak absorption band centred at 1,820 Å.[127] Later two strong bands were observed at about 1,350 and 1,200 Å respectively.[112] It has been suggested that the weak band is due to a forbidden $\sigma \rightarrow \pi^*$ transition, and that the two strong bands arise respectively from $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions.[128]

ELECTRON-DIFFRACTION STUDIES

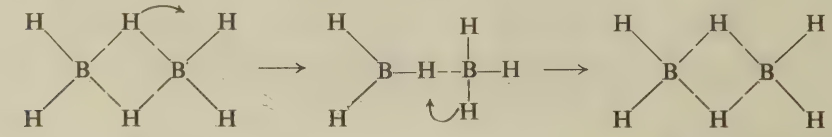
Early electron-diffraction experiments[83] were instrumental for the selection of the correct basic structure of diborane(6). Since then, improved measurements[90] have provided precise molecular parameters that are incorporated in Table II. Estimates of the mean amplitudes of atomic vibrations in diborane(6) have also been made.[90]

NUCLEAR-MAGNETIC-RESONANCE SPECTRA

Much n.m.r. work has been carried out since the time of the early interpretative work of the proton magnetic resonances of diborane(6).[129–31] These studies have confirmed the structure already discussed, that is, they accord with the presence of two sterically non-equivalent kinds of hydrogen atoms in the ratio 2:1 and complete geometrical equivalence of the boron atoms. Since both the hydrogen and boron nuclei have non-zero spin moments, the resonances of each can be studied, but extensive spin-spin coupling between the boron atoms and the protons—particularly strong in the case of the terminal protons—is a complicating factor. For ^{11}B spectra this observed coupling can be eliminated and the spectrum simplified by paramagnetic metal ions in their S states[132] or by replacing the hydrogen with deuterium. For proton spectra, considerable simplification is effected by scrambling the boron nuclei with an appropriate applied signal[133], whereupon the fine structure due to their spin orientation collapses. The resonances for the bridge protons are found at higher fields than those of the terminal protons.[134]

The bridge protons give rise to a characteristic feature in the spectrum. Considerable interest is attached to the spectrum of the bridge protons that is theoretically a septet of intensity ratio 1:2:3:4:3:2:1; this ratio is a reflection of the statistical weights of the possible combined spins of the two ^{11}B nuclei, each of spin $\frac{3}{2}$. These nuclei may mutually orient themselves to give any one of seven different values for the combined spin (viz., -3, -2, -1, 0, 1, 2, 3, respectively) weighted statistically as stated. At the low operating frequencies originally used for the proton spectra[129, 131], the peaks of the septet are in part seriously masked by a wider spaced and more intense quartet from the terminal protons, but the septet may be largely or completely shifted away by operating at 60 or 100 MHz respectively. Furthermore, with high resolution, long-range spin coupling between the bridge and terminal protons can be observed.[135–6] (Diborane(6) is probably the only boron hydride in which such coupling is strong enough to be resolved.)

The more obvious features of the ^{11}B spectrum for diborane(6) are fundamentally simple and consist of a triplet of triplets, which is comprised of a large triplet structure arising from the terminal BH_2 groups associated with a much smaller triplet splitting due to interaction with the bridge hydrogen atoms. These features are preserved at elevated pressures and temperatures[137], but certain solvents such as ethers change the spectrum in such a way that the bridge and terminal hydrogen atoms tend to become magnetically equivalent. Thus in diethyl ether solution diborane shows the usual triplet of triplets at low temperatures, but at higher temperatures this simplifies to a 7-line multiplet[138], which has been attributed to more rapid intramolecular proton exchange. Conceivably this can be depicted as a pseudorotation of a BH_3 group:



In this scheme the unstable intermediate form could derive greater stability through interaction with a solvent molecule acting as a transient donor at the boron atom appearing on the left. Thus in diethyl ether the energy barrier is reduced to 4·8 kcal mol^{-1}, whereas with the polyether diglyme as solvent it is reduced still further, since the change in the spectrum is complete at lower temperatures.[138]

Under high resolution the ^{11}B spectrum is considerably more elaborate because the $^{11}B_2H_6$ nuclear spin system is strictly of the $A_2A'_2M_2XX'$ type, in which the two ^{11}B nuclei (X, X′) are magnetically non-equivalent owing to different magnitudes of spin-spin interactions with the terminal protons (A, A′). Accordingly the spin-spin coupling of the boron nuclei is observed in the high-resolution spectrum.[136] An upper limit of 1·1 Hz has been determined for J_{BB}.[139]

The resonance spectrum of the ^{10}B nucleus (spin moment 3) has also been observed[135] for $^{10}B_2H_6$ of 96% ^{10}B isotopic purity and a brief but convincing explanation has been given. Both ^{10}B and ^{11}B nuclear spin-lattice relaxation times have been measured for diborane(6).[140] Chemical shifts and coupling constants are given in Table V. Comparison has been made with the values for other boron compounds.[141]

Table V.—Chemical Shifts and Coupling Constants for Diborane(6)$^{(a)}$

Isotopic composition	Nucleus	BH_2		HBH		$H_b \cdots H_t$
		δ	*J* (Hz)	δ	*J* (Hz)	*J* (Hz)
Isotopically normal	$^{1}H^{(b)}$	−3·95	135±2	+0·53	46·1	7·0
	$^{11}B^{(c)}$	−17·5	135±2		46±2	
96% ^{10}B	$^{1}H^{(b)}$	−3·95	44·5±1	+0·43±0·1	15	7
	^{10}B		44·5±1		15·1±0·5	

(a) Values from Ref. 135.
(b) Chemical shifts in p.p.m. relative to $SiMe_4$.
(c) Chemical shifts in p.p.m. relative to $Et_2O.BF_3$.

PHOTOELECTRON SPECTRUM

Three independent attempts have been made to study diborane(6) by means of photoelectron spectroscopy.[142–3, 128] Special interest is associated with the energies of the electrons participating in the 3-centre bonds. It seems clear that five different ionization potentials below 20 eV are observed, in agreement with theoretical prediction, and both adiabatic and vertical values have been published. But whereas the three sets of results agree satisfactorily for some values, there are points of appreciable difference, both experimental and interpretative. Nevertheless, the method gives unambiguously a first ionization potential (adiabatic) of *c.* 11·4 eV associated with a terminal bonding electron, which is thus less tightly held than an electron in the bridge bond, with an experimental value of 12·728[142] or *c.* 14·42[143] eV (adiabatic), depending on the interpretation.

MASS SPECTRUM

The mass spectrum of diborane(6) has been independently examined by a number of different workers.[8–10, 144–6] The mass-spectral patterns for B_2D_6[14–15] and a number of partially deuterated diboranes[15] have also been investigated. Because the results are intimately connected with fragmentation by electron impact, they are discussed in the section that deals with that topic on p. 81.

BOND ENERGIES AND BOND PROPERTIES

Notwithstanding the fact that diborane(6) is thermodynamically unstable with respect to elemental boron and hydrogen, attempts to detonate it have failed.[147] The reason may lie in the fact that it is only mildly endothermic. Deuterodiborane B_2D_6 is about 4·5 kcal mol^{-1} less endothermic than B_2H_6 itself.[148–51] It would follow that the bonding is slightly stronger in the deutero compound. Determinations of the enthalpy of formation ΔH_f of diborane are in only fair agreement, but, allowing 0·9 kcal mol^{-1} for the heat of transformation of amorphous boron to the crystalline β form, most of the modern determinations[148–54] place ΔH_f for B_2H_6 within the range 8·5 ± 1 kcal mol^{-1}.[155]

This value for ΔH_f corresponds to 573·1 kcal mol^{-1} for the atomic heat of formation. The limits of error in this figure are enhanced by uncertainty in the value adopted for the heat of atomization of boron, viz., 134·5 kcal mol^{-1}.[155] Since there are two types of hydrogen atoms, this energy cannot be unequivocally divided between the bonds to give the individual bond energies. It is not possible to obtain a unique value for, say, the terminal B—H bond energy in diborane. All that can be concluded is that it will be less than one-sixth (i.e. $< 95{\cdot}6$ kcal mol^{-1}) of the atomic heat of formation of the molecule as a whole, since this consists of two BH_3 groups condensed and the total atomic heat of formation includes the energy liberated on association. A knowledge of the dissociation energy of the bridge bond would however enable a unique value to be obtained for the B—H bond energy in BH_3.

A least-squares calculation of the potential constants[97] has indicated that the stretching force constant of a bridge B—H$_b$ bond is about half that of a terminal B—H$_t$ bond. Other calculations of the force constants and potential-energy constants have been made[156, 116], but they have not yet been repeated with the improved vibrational assignments and molecular parameters referred to above. Mean-square vibrational amplitudes have been studied[90, 157, 94–5], and it has been shown that those for the bridge hydrogen atoms exceed those for the terminal atoms.

BRIDGE-BOND DISSOCIATION ENERGY

Although the energy of dissociation of diborane(6) into two BH_3 molecules is a matter of great interest, all attempts to measure this quantity directly from a study of the supposed equilibrium

$$B_2H_6 \rightleftharpoons 2BH_3$$

have failed. Indeed, in spite of numerous attempts by a variety of methods, the presence in any measurable concentration of free BH_3 in equilibrium with diborane at elevated temperatures has never been directly demonstrated, and the validity of all earlier claims to have done so must now be doubted. For example, BH_3 has escaped identification in the ^{11}B n.m.r. spectrum of diborane at temperatures up to 123°C[137], that is, to a point only just below that where the pyrolysis becomes rapid. Accordingly it has latterly been concluded[18] that diborane(6) does not dissociate reversibly and that, once BH_3 appears, it preferentially reacts with the endothermic diborane by a mechanism that is sufficiently rapid to prevent a measurable concentration of BH_3 from being built up. This is not to say that the BH_3 molecule is intrinsically incapable of existence. Unless it exists as a transitory species, it would be very difficult, for example, to explain the kinetics of the interconversion of boranes at elevated temperatures. Also, the species BH_3^+ has been detected by mass spectrometry in recent studies of the pyrolysis of diborane[158–60] under conditions that give quite good indirect evidence for the short-lived existence of neutral BH_3.

Since, however, a direct study of the equilibrium is not feasible, the bridge-bond dissociation energy $D(H_3B\cdots BH_3)$ must be estimated by less direct means. Several such methods are now available, but they have not led to concordant results. Although limits had already been proposed, namely 15[88] and ~50 kcal mol^{-1} [161], the first serious attempt to fix D more precisely was one which, by incorporating certain assumptions, led to the value 28·5 kcal mol^{-1} from the heats of reaction of B_2H_6 and $B_2H_2Me_4$ with gaseous methylamines.[162–3] More recently the limits $38{\cdot}3 > D > 32$ kcal mol^{-1} have been calculated from the kinetics of decomposition of borane carbonyl BH_3CO and an assumed mechanism[164], whereas similar treatment of the data for BH_3PF_3 has led to $D = 35{\cdot}0$ kcal mol^{-1}.[165] However, both estimates are based on mechanisms in which the simple association of $2BH_3$ to B_2H_6 is an assumed step, whereas, as has been noted above, BH_3 disappears preferentially in an alternative manner (see also p. 135). Other estimates based on kinetic studies of borane carbonyl with added triethylamine and, in a flow system, without this additive are upper limits of 33·5 ± 2·4[166] and 36 ± 3 kcal mol^{-1} [167] respectively, both being based on supposed equilibrium data.[168] Recent electron-impact studies have provided the estimates 37[158], 37·1 ± 4[169], 55 ± 8[159] (later unsubstantiated[160]), 59[74] and 59 kcal mol^{-1} [170] respectively for D. On the other hand, the temperature variation of the disproportionation equilibrium of $B_2H_2Me_4$ has been studied[171], and this is in accord with the much lower estimate of 18·4 kcal mol^{-1} for $D(Me_2BH\cdots HBMe_2)$.[172] There is no reason to expect the bridge-bond dissociation energies for B_2H_6 and $B_2H_2Me_4$ to differ by any large amount. Furthermore, the only published estimate of the difference, which rests on assumed values for the entropies of the methyldiboranes and rather imprecise equilibrium data, shows B_2H_6 to have a bridge-bond dissociation energy 3·5 kcal mol^{-1} higher than that of $B_2H_2Me_4$. The previously cited value for $D(Me_2BH\cdots HBMe_2)$ thus corresponds to *c*. 22 kcal mol^{-1} for $D(H_3B\cdots BH_3)$. Admittedly the precision must remain low until the spread in the dissociation energies of the methyldiboranes is more accurately known, but the approach is fundamentally sound, in that it does not rest on assumed mechanisms but depends on strictly reversible equilibria that involve the stable molecule trimethylborane BMe_3 in place of the highly reactive species BH_3, whose equilibrium concentration cannot be measured. Accordingly, the value may be expected to be of the right order. It is truly a net dissociation energy, whereas the much higher, non-equilibrium value of 59 kcal mol^{-1} obtained from electron-impact studies is strictly a gross dissociation energy. The two values are reconcilable if the dissociation process involves a considerable potential hill, which, theoretically[18] at least, is quite possible. Their difference may legitimately be regarded as providing confirmatory evidence for this phenomenon, which had already been proposed to explain the mechanism of photolytic decomposition of diborane.[68]

General Physical Properties

Diborane(6) is a colourless compound of limited stability, and is a gas at room temperature. There are at least two solid modifications, a low-temperature α form and a high-temperature β form, the reported transition temperature lying in the neighbourhood of 60 K. However, annealing at 90 K is necessary to effect the transformation, since the two modifications can co-exist over a range of temperature. The structure of the β phase has been determined.[173] Evidence for the existence of a third solid phase has since been found in the results of polarized infra-red spectroscopic studies of solid B_2H_6, which have been used to elucidate the main features of the structure of the low-temperature modification.[119]

The m.p. of diborane(6) is $-164{\cdot}86$°C, and the b.p. $-92{\cdot}53$°C.[174]

The variation with temperature of the vapour pressures of diborane(6) and its hexadeutero derivative has been extensively studied.[175–6] By means of least-squares fits, the following vapour-pressure equations for pressures below 1 atm have been derived[175]:

$$B_2H_6\colon \log_{10} p_{\mathrm{Torr}} = -974{\cdot}156/T - 0{\cdot}00653809T + 9{\cdot}45290$$

$$B_2D_6\colon \log_{10} p_{\mathrm{Torr}} = -962{\cdot}893/T - 0{\cdot}00601480T + 9{\cdot}31798$$

Deuterodiborane(6) has a b.p. *c.* 0·9°C lower than B_2H_6, although its heat of vaporization at the b.p. is 35 cal mol^{-1} higher. Above atmospheric pressure, the vapour pressure of B_2H_6 is more accurately represented by the relation[176]

$$\log_{10} p_{\mathrm{atm}} = 4{\cdot}8600 - 1{,}236{\cdot}2/T + 122{,}150/T^2 - 12{,}247{,}000/T^3 + 341{,}410{,}000/T^4$$

Diborane(6) has the distinction of being one of the very few substances for which the heat of vaporization has been measured calorimetrically for almost the entire liquid range, that is, to within 4°C of the critical point.[177] The experimental values are reproduced quite well by the expression

$$\Delta H_v = 546{\cdot}2(T_c - T)^{0{\cdot}39} \text{ cal mol}^{-1}$$

From these results, the entropy of vaporization has been calculated over a temperature range extending up to the critical point. Values for the vapour pressure and enthalpy and entropy of vaporization as smoothed from the available experimental data[178] are reproduced in Table VI.

Tabulations of thermodynamic data for diborane(6) treated as an ideal gas have been published[179–80], but the most comprehensive tabulation for the liquid and real gas, both below and above the critical temperature, is still one based on the best experimental data available in 1959[178]: this comprehends a wide range of temperature and pressure for the densities of liquid and vapour, enthalpy, entropy and Gibbs free energy of vaporization, compression factor, specific heat at constant pressure, specific-heat ratio, and Joule–Thomson coefficient, as well as the critical constants and an equation of state. Some selected thermodynamic data for B_2H_6 are reproduced in Table VII. Other values published for the liquid density[181] and molar volume[181–2] are not in very good agreement, and may be less accurate. It is interesting to note that the significant structure theory of the liquid predicts physical properties that are in good agreement with the experimental values for the vapour pressure, molar volume, entropy, critical constants, heat capacity, coefficient of thermal expansion and compressibility.[183] Other experimentally determined properties for the liquid are the surface tension[184], dielectric

Table VI.—Enthalpy of Vaporization and Entropy of Vaporization of Diborane(6)(a)

Temperature (K)	Vapour pressure (atm)	ΔH_v (kcal mol^{-1})	ΔS_v (cal mol^{-1} K^{-1})
130	0·01672	3·942	30·32
140	0·04920	3·837	27·41
150	0·1228	3·738	24·92
160	0·2693	3·639	22·74
170	0·5318	3·537	20·80
180	0·9649	3·429	19·05
180·63	1·000	3·422	18·94
190	1·633	3·313	17·43
200	2·606	3·187	15·93
210	3·963	3·050	14·52
220	5·785	2·899	13·18
230	8·154	2·733	11·88
240	11·16	2·548	10·62
250	14·90	2·337	9·35
260	19·47	2·089	8·04
270	25·01	1·778	6·59
273·15	26·97	1·659	6·07
280	31·66	1·337	4·78
284	34·68	1·074	3·78
286	36·27	0·898	3·14
288	37·93	0·651	2·26
289·85	39·52	0·000	0·00

(a) From Ref. 178.

Table VII.—Selected Thermodynamic Data for Diborane(6) (real gas) at 1 Atm Pressure(a)

T (K)	C°_p (cal mol^{-1} K^{-1})	$-(G^\circ - H^\circ_0)/T$ (kcal mol^{-1})	S° (cal mol^{-1} K^{-1})	$(H^\circ - H^\circ_0)/T$ (kcal mol^{-1})
180·66	10·363(b)	41·657(b)	49·658(b)	8·000(b)
190	10·449	42·049	50·165	8·118
200	10·598	42·454	50·691	8·236
220	11·025	43·233	51·703	8·469
250	11·885	44·320	53·147	8·827
273·15	12·658	45·107	54·226	9·117
298·15	13·549	45·916	55·367	9·451
300	13·616	45·974	55·451	9·477
400	17·302	48·889	59·862	10·973
500	20·740	51·506	64·095	12·589
1,000	32·347	62·596	82·526	19·932
1,500	37·528	71·713	96·762	25·049

(a) Derived from Ref. 178.
(b) Value for the b.p. added by extrapolation.

constant[174] and diamagnetic susceptibility[185]; those for the gas include the second virial coefficient[186–7] (see Table VIII), the thermal conductivity[188], and the viscosity[188–9], from which the Lennard–Jones potential of intermolecular interaction has been calculated and values of 4·821 and 213·2 derived for the intermolecular force constants σ and ϵ/k respectively.[189] The numerical values for some of the physical properties of diborane are listed in Table IX.

The solubility of hydrogen in liquid diborane(6) has been measured for the temperature range 112·08–181·73 K and for pressures up to 41·69 atm.[191] The results are unusual, in that the solubility of the hydrogen is observed to increase with temperature. The Henry's Law constant k, expressed in reciprocal atmospheres, is given to within 1% by the relation

$$\log k = 6{\cdot}704 + 7{\cdot}618/T - 1{\cdot}581 \log T$$

Table VIII.—Second Virial Coefficient of Diborane(6)

T (K)	$B^{(a)}$ (cm^3 mol^{-1})
113·12	−1,385·5
124·10	−1,179·5
134·95	−1,018·1
146·21	−886·2
158·31	−768·7
169·78	−676·5
181·58	−597·1
273·15	−227$^{(b)}$

(a) Values from Ref. 186, except where otherwise indicated.
(b) Value from Ref. 187.

Table IX.—Physical and Physicochemical Properties of Diborane(6)

Property	Numerical value	Units	Ref.
M.p.	−164·86	°C	174
B.p., T_b	−92·53	°C	174
Dielectric constant of liquid	$2{\cdot}3721 - 0{\cdot}0027653T$		174
Surface tension (−120·3°C)	18·32	dyne cm^{-1}	184
Magnetic susceptibility	$-2{\cdot}1 \times 10^{-5}$		185
Molar volume (T_b, 1 atm)	64·67	cm^3 mol^{-1}	(178)
Density of liquid (T_b, 1 atm)	$428{\cdot}2 \times 10^{-3}$	g cm^{-3}	178
Density of gas (T_b, 1 atm)	$1{\cdot}947 \times 10^{-3}$	g cm^{-3}	178
Critical density	$165{\cdot}8 \times 10^{-3}$	g cm^{-3}	178
Critical temperature, T_c	16·7	°C	178
Critical pressure, p_c	39·52	atm	178
Critical volume	166·9	cm^3 mol^{-1}	(178)
Compression factor (T_c, p_c)	0·2775		178
Compression factor (25°C, 1 atm)	0·9921		178
Enthalpy of vaporization (T_b, 1 atm)	3,422	cal mol^{-1}	178
Entropy of vaporization (T_b, 1 atm)	18·94	cal mol^{-1} K^{-1}	178
$H^\circ_{298\cdot15} - H^\circ_0$	2·857	kcal mol^{-1}	155
Entropy (25°C, 1 atm)	55·45	cal mol^{-1} K^{-1}	155
Specific heat, C_p (25°C, 1 atm)	13·60	cal mol^{-1} K^{-1}	155
Ratio C_p/C_V (25°C, 1 atm)	1·1790		178
Joule–Thomson coefficient (25°C, 1 atm)	1·1088	K atm^{-1}	178
Thermal conductivity (26·85°C, 1 atm)	$52{\cdot}0 \times 10^{-6}$	cal cm^{-1} s^{-1} K^{-1}	188
Viscosity (26·85°C, 1 atm)	$77{\cdot}6 \times 10^{-6}$	dyne s cm^{-2}	188
Enthalpy of formation (25°C, 1 atm)	8·5	kcal mol^{-1}	155
Gibbs free energy of formation (25°C, 1 atm)	20·7	kcal mol^{-1}	155
Entropy of formation (25°C, 1 atm)	−40·97	cal mol^{-1} K^{-1}	(155, 190)

while the partial molal enthalpy of solution at infinite dilution $\Delta\bar{H}_s$ is given by the expression

$$\Delta\bar{H}_s = (30{\cdot}68 - 3{\cdot}141T)\ \text{cal mol}^{-1}$$

Some values are given in Table X. The partial molal volume of the hydrogen in solution is *c.* 20 cm^3, which is 8 cm^3 less than the molal volume of liquid hydrogen at its boiling point.

The solubility of gaseous diborane(6) in a number of solvents has been extensively investigated. With diethyl ether as solvent, the deviation from Raoult's Law is positive.[192] At 25°C, 100 g of diethyl ether dissolves 1·1 g of B_2H_6 at 1 atm pressure, while 100 g of tetrahydrofuran dissolves 8·1 g under the same conditions.[193] Tetrahydrofuran is thus a much more useful solvent for diborane(6). Of particular importance because

Refs. p. 144

Table X.—The Solubility of Hydrogen in Liquid Diborane(6): Henry's Law Constants and Enthalpies of Solution at Various Temperatures[a]

T (K)	Henry's Law constant $k^{(b)}$ (atm^{-1})	Enthalpy of solution $\Delta\bar{H}_s^{(c)}$ (cal mol^{-1})
113·12	3,349	386
124·10	2,853	420
134·95	2,471	455
146·21	2,155	490
158·31	1,883	528
169·78	1,674	564
181·58	1,442	601

(a) Values from Ref. 191.

(b) Extrapolated to conditions for which $(p-p_0)=0$, where p is the total pressure and p_0 the vapour pressure of pure diborane(6) at the temperature of the isotherm.

(c) The partial molal enthalpy of solution at infinite dilution.

of the practical significance of the system are the studies[194–5] with the polyether diglyme as solvent, 100 g of which dissolves 0·7 g of B_2H_6 at 1 atm pressure and 25°C. Solubility measurements have also been conducted in *n*-butane[196], *n*-pentane[196–7], di-*t*-butylsulphide[194], furfural[198], nitrobenzene[198] and tetraethoxysilane[198], among other substances.

Handling and Physiological Properties

Although special care is demanded, no major difficulties are associated with the handling of diborane(6). The principal hazards arise from its toxicity and its reactivity and relative instability—reports of spontaneous ignition and detonation do not[147] refer to the pure compound, which has a flash point of 145°C in air, associated with the wide flammability limits of 0·8 and 98% by volume.[199]

Diborane is considerably less toxic than pentaborane(9), but the extent to which this is due to its much faster rate of hydrolysis by atmospheric moisture is not known. In the rare cases of accidental poisoning the reported symptoms are tightness of the chest, coughing and headache, accompanied sometimes by nausea, chills, dizziness and lethargy. The symptons usually disappear quickly after the exposure has ended. Unlike pentaborane, diborane has little or no effect on the central nervous system[200], but, as has been learned from experiments with animals, the physiological effect on the lungs is similar to that of phosgene. Oxygen therapy is therefore indicated in cases of severe diborane poisoning. A protective gas mask has been developed[201], as have monitoring devices.[202–3] Other safety precautions have been discussed.[199] The rather unpleasant, chocolate-like odour of diborane is not an adequate safeguard against dangerous concentrations, because, although the body can tolerate concentrations of 0·1 p.p.m., symptoms appear at concentrations below that at which a smell becomes detectable, namely 3–4 p.p.m. Work with animals has been usefully summarized[204], and here it will suffice as a general indication to note that the exposure of mature rats to a dose of 80 p.p.m. for 4 hours causes a mortality of 50%.[205]

All the above difficulties of handling are readily overcome by working with isolated systems. For purifying diborane, ordinary vacuum fractionation at low temperatures is completely adequate provided that it is merely necessary to remove other boranes. The presence of other contaminants, such as low-boiling hydrocarbons or other gases, may require resort either to specialized vacuum stills or to chemical separation. A highly sensitive separation has been described[206] which makes use of a Le Roy still.[207] Separation from substances such as ethane can be effected by the use of active charcoal, from which the diborane may be subsequently displaced by boron trifluoride or trichloride.[208] Chemical separation usually involves the formation of a borane complex with, for example, pyridine[209] or dimethyl sulphide[210], from complexes of which regeneration of diborane results on treatment with boron trifluoride or zinc chloride respectively.

In some countries diborane has long been sold commercially in cylinders which need to be kept refrigerated, or as solutions in inert solvents, or occasionally as mixtures with other gases such as hydrogen or argon. The use of argon has little to be said in its favour, but hydrogen retards decomposition.[161]

Preparation

A great variety of methods for preparing diborane(6) is now known. The original method due to Stock[81] depended on the pyrolysis of tetraborane(10), which in turn was prepared by the action of aqueous acids on magnesium boride, itself an inconvenient substance to prepare. Overall yields of diborane were minute, and indeed it may be said that preparative difficulties were mainly responsible for the comparatively slow advance in diborane chemistry for almost 40 years. The preparative breakthrough came only after lithium aluminium hydride and, later, tetrahydroborates became readily available a few years after the end of the Second World War, and the first procedure that led to a moderately good yield of diborane(6) appeared in print in 1951. Since then the search for more efficient ways of preparation has continued, and by 1956 sufficient information on the preparation of diborane had accumulated to warrant a special review, although this did not appear in print until 1961.[211] Some further information appears in articles and treatises dealing with the boranes as a whole[3, 212–14], but none of these is comprehensive.

In the following account it is convenient to classify the methods into six main types. Except for the first two types, all involve either reducing agents or some kind of electrolytic reduction, and can be further subdivided according to the chemical form in which the boron is introduced. Whereas some methods involve single-stage processes, others require two or more stages, though no attempt is made to classify them on such a basis. The choice of method will still largely depend upon individual requirements, but the general picture has changed considerably now that metal tetrahydroborates (borohydrides) are commercially available. Particularly since alkali metal tetrahydroborates have become relatively cheap[215], the emphasis has shifted to ways of utilizing them as the starting material. Accordingly, on account of their increasing importance, such methods are considered first.

FROM METAL TETRAHYDROBORATES

Bearing in mind the close relationship between diborane(6) and borane(3) BH_3, which may be regarded as a unit that is already preformed in tetrahydroborates, the latter compounds promised, and have proved in practice, to be an excellent source of B_2H_6. Metal tetrahydroborates have been the subject of a recent review[216] and a section in this Supplement is devoted to them (p. 354). A variety of methods for releasing diborane from them is now known, although aqueous and hydroxylic reagents that react with the product are useless. However, most of the reported methods suffer from one or more avoidable practical disadvantages.

The reaction of boron trifluoride etherate with a solution of lithium tetrahydroborate in a simple ether or in dioxane[217–18] is of importance, not only as the first reaction of this kind to be discovered, but also as the first reaction of any kind found to produce diborane in moderately good yield since the compound was first isolated and characterized by Stock. In the absence of a solvent, gaseous boron trifluoride does not react appreciably, but the reaction with the etherate is rapid and may be written

$$3LiBH_4 + BF_3.OEt_2 \xrightarrow{Et_2O} 2B_2H_6 + 3LiF + Et_2O$$

In pilot-plant trials a 90·9% yield of diborane (purity 95%) was obtained[219], although under ordinary laboratory conditions this is rarely achieved. The reaction can also be carried out in tetrahydrofuran, but the yield is much lower.[220] Instead of the etherate

$BF_3.Et_2O$, lithium tetrafluoroborate in ether may be employed with good results[220], although the reaction appears to be reversible[147]:

$$3LiBH_4+LiBF_4 \overset{Et_2O}{\rightleftharpoons} 2B_2H_6+4LiF$$

There is however a major disadvantage in using boron trifluoride or tetrafluoroborates in the preparation of diborane, since they result in a product that is contaminated with boron trifluoride, which is not readily removed.[221] Particularly when the diborane is required for selective reductions, that is a most undesirable impurity: traces of BF_3 enhance the reducing powers of B_2H_6 and catalyze hydrogenolysis at centres that would not otherwise be attacked.[222]

Methods employing volatile ethers also suffer from another serious disadvantage, in that the product is contaminated with ether vapours which cannot be removed without vacuum fractionation, or at least severe refrigeration. Some cleavage of the ether can also occur, and one particularly troublesome by-product may be ethyl fluoride.[223] With boron trichloride or tribromide, ether cleavage is even more pronounced. The by-product is then usually ethane, which also has a volatility similar to that of diborane. Replacing the ether by a solvent such as benzene or toluene is a feasible way of overcoming the difficulty, but the presence of aluminium chloride or bromide is required, and even then the reaction is slow below 63°C.[224] A similar cleavage problem is encountered when hydrogen iodide is used to decompose the lithium tetrahydroborate, but again it may be avoided by using toluene instead of ether as solvent.[225] Certain transition metal halides will also decompose $LiBH_4$ in ether, and the reactions with ferric chloride[226] and cupric chloride[227] have been investigated. The equations as reported are:

$$3LiBH_4+FeCl_3 \xrightarrow{\text{ether}} 3LiCl+\tfrac{1}{2}B_2H_6+4\tfrac{1}{2}H_2+Fe+2B$$

$$2LiBH_4+CuCl_2 \xrightarrow{\text{ether}} 2LiCl+B_2H_6+H_2+Cu$$

The iron is left as a black pyrophoric residue. An interesting feature of these reactions is that the tetrahydroborates $Fe(BH_4)_2$ and $CuBH_4$, which can be isolated at reduced temperatures, reportedly decompose into the metal, diborane and hydrogen on warming to about −10°C, thus throwing doubt on the correctness of the right-hand side of the above equation for the reaction with $FeCl_3$.

Owing to their very much lower reactivity and, to a lesser extent, their relative insolubility in simple ethers, the tetrahydroborates of sodium and potassium will not participate in many of the above-mentioned reactions of the lithium salt. But because it is so much cheaper and is easier to handle, the sodium salt in particular has received much study.[216] Generally yields are lower, but in ether suspension $NaBH_4$ will give diborane with $BF_3.Et_2O$[218] or $FeCl_3$[228], and in the vapour state the latter substance is also effective in the absence of ether at 220°–320°C:

$$2NaBH_4+2FeCl_3 \rightarrow B_2H_6+H_2+2NaCl+2FeCl_2$$

On the other hand, with BCl_3 vapour $NaBH_4$ gives no reaction, even under pressure at 185°C[229], although $LiBH_4$ reacts to completion at 145°C and even commences to react at room temperature.[171] For $NaBH_4$ to react with BF_3 or BCl_3, temperatures of 220° and 250°C respectively are needed.[230] However, in the presence of aluminium chloride in a hydrocarbon solvent such as toluene, it can be induced to react at 55°C.[231] The less reactive KBH_4 will also react with $BF_3.Et_2O$ or BCl_3 in the presence of certain metal halides such as $AlCl_3$.[232]

An important advance was the discovery that sodium tetrahydroborate is soluble in polyethers, in particular the dimethyl ethers of the polyethylene glycols[233,211], of which the following (especially the second) are the most commonly used:

ether	trivial name
Ethylene glycol dimethyl ether	Glyme
Diethylene glycol dimethyl ether	Diglyme
Triethylene glycol dimethyl ether	Triglyme

These ethers have much lower volatilities, which is an added advantage. With these discoveries it became feasible to obtain a good yield of diborane from $NaBH_4$ and BF_3[234] or $BF_3.Et_2O$[235], even in solvents in which the sodium salt is insoluble, provided it was admixed with a few per cent of diglyme. The potassium salt also gives a fair yield in diglyme solution.[199] A disadvantage of this process is that not all the boron is converted to diborane, but part of it remains in suspension as the alkali metal tetrafluoroborate

$$3MBH_4 + 4BF_3 \xrightarrow{\text{diglyme}} 2B_2H_6 + 3MBF_4 \quad [M = Na, K]$$

The sodium and potassium salts therefore require four times as much boron trifluoride as does $LiBH_4$, which is converted to LiF. Conceivably this difficulty could be overcome by the prior addition of an equimolecular quantity of lithium chloride, bromide or iodide, since other cases are known in which lithium halides affect the reactions of $NaBH_4$[236, 233], presumably because $LiBH_4$ is formed by metathesis[237]: the point does not appear to have been put to experimental test, however.

An additional inconvenience is that $NaBH_4$ and KBH_4 do not evolve the diborane(6) evenly in solvents such as diglyme: they only begin to release it in the latter stages of the reaction when a large part of the reactant has been added. In the case of the sodium salt, this is known to be largely due to the formation of sodium heptahydrodiborate NaB_2H_7 in solution, apparently through the addition of BH_3 to unreacted $NaBH_4$[238], so that the reaction proceeds in two stages[234]:

$$7NaBH_4 + 4BF_3 \xrightarrow{\text{diglyme}} 4NaB_2H_7 + 3NaBF_4$$

$$6NaB_2H_7 + 8BF_3 \xrightarrow{\text{diglyme}} 7B_2H_6 + 6NaBF_4$$

With the lithium salt, LiB_2H_7 has been assumed to be formed in diglyme solution[239]; but since there is evidence that KB_2H_7 is not formed with KBH_4 under like conditions[211, 199], another explanation must be sought in this case.

Instead of boron trifluoride, either BCl_3 or $B(OMe)_2Cl$ will release diborane(6) from $NaBH_4$ in diglyme, but on a pilot-plant scale it was found that BCl_3 effects excessive ether cleavage[211]: excess of the chloride is to be avoided even on a laboratory scale, since it reduces the yield until the diborane vanishes when the molar ratio $BCl_3:NaBH_4$ becomes equal to unity[234], a fact that has been ascribed to the formation of relatively stable chloroborane etherates:

$$NaBH_4 + BCl_3 + 2R_2O \rightarrow NaCl + 2H_2BCl.OR_2$$

Although trimethyl and triphenyl borates fail even at 200°C to give any diborane with $NaBH_4$ in diglyme[239], trialkylboroxines are quite effective in releasing diborane[240], as is dimethyl sulphate.[241] Higher boranes such as tetraborane[242] and decaborane[243] also produce B_2H_6 by interaction with $NaBH_4$ in glyme. In the former case, the tetraborane contributes one BH_3 group to the B_2H_6 molecule, so that the method can be utilized for preparing partially deuterated diborane from $NaBD_4$:

$$NaBD_4 + B_4H_{10} \rightarrow NaB_3H_7D + B_2H_3D_3$$

Diborane is also liberated when solutions of $NaBH_4$ and other tetrahydroborates are electrolyzed in an inert solvent, e.g. in one of the N,N-dialkylformamides[244] or in a polyglyme.[245] In diglyme it is the only borane to appear, but the method has not found general favour because NaB_2H_7 formation hinders the liberation of diborane until half of the required current has passed; and, more important, the sodium liberated at the cathode tends to float on the solvent and cause an internal short-circuit unless a mercury cathode is used. Because $NaBH_4$ is also soluble in a melt of mixed metal chlorides (e.g. $LiCl + NaCl + KCl + AlCl_3$), at elevated temperatures such a medium may also be employed as flux in electrolytic preparation[245], but higher boranes then contaminate the product, especially above 250°C. In a halide melt chemical liberation of diborane can alternatively be effected by acid gases such as BF_3 or HCl.[246–7]

In general, however, such gases are not convenient to use for liberating diborane, and whether anhydrous hydrogen halides react at all depends both on the identity of the halogen and on that of the metal in the tetrahydroborate, and sometimes on solvent effects as well. Thus $NaBH_4$ will not react with gaseous HCl, even at 180°C under pressure[171], although $LiBH_4$ gives B_2H_6 at $-80°C$[248], as does $Mg(BH_4)_2$ at low temperatures with a solution of HCl in ether.[249] On the other hand, $NaBH_4$ readily reacts with HI in ether or hexane.[225]Generally speaking, the use of ethers is liable to introduce cleavage problems, and the use of alcohols as solvents also causes side reactions. Thus HCl dissolved in methanol apparently produces $BH(OMe)_2$ along with B_2H_6 on reacting with $LiBH_4$.[250]

Anhydrous acids of sufficient resistance to reduction will liberate B_2H_6 from $NaBH_4$. Thus concentrated H_2SO_4 will do so in the absence of a solvent or (with advantage) in a chlorobenzene.[251–2] However, it has been shown that partial reduction of the acid to SO_2 and even H_2S occurs, although this difficulty can be avoided if the H_2SO_4 is replaced by methanesulphonic acid.[253] Alternatively it is possible to utilize chlorosulphonic acid[252], concentrated phosphoric acid (40–70% yield with KBH_4)[254–5], or anhydrous fluorophosphoric acid (79% yield with $NaBH_4$ under vacuum).[256] However, acids have the disadvantage that they normally give rise to a product contaminated with carbon dioxide from the carbonate almost inevitably present as an impurity in the solid tetrahydroborate used as starting material. Esters of tetrafluoroboric acid such as F_2BOMe also give good yields with $NaBH_4$ in tetrahydrofuran[257], although, as mentioned previously, this solvent is generally less favourable than a simple dialkyl ether. Tetrahydrofuran can also be used for the preparation of B_2H_6 from $Ca(BH_4)_2$ and BF_3[258] or BCl_3.[259]

Towards bromine and iodine, the behaviour of the various tetrahydroborates differs. Although $NaBH_4$ does not react with Br_2 even at 80°C[225], the potassium salt reacts at room temperature in the absence of a solvent to give a 90% yield of diborane(6)[260]:

$$2KBH_4+2Br_2 \rightarrow B_2H_6+2HBr+2KBr$$

The HBr produced simultaneously is a major inconvenience, and some boron tribromide and hydrogen are formed at the same time. In the absence of a solvent $LiBH_4$ reacts with I_2, but not to give diborane[225]; however, in hexane, heptane or octane some B_2H_6 is released, and larger quantities with $NaBH_4$ or KBH_4.[260] In diglyme solution the reaction proceeds differently (see below): no hydrogen halide is formed and the yield of diborane may amount to 98%.

It is surprising that the action of the halides of the *b*-subgroup elements of groups II–IV was not investigated earlier, especially since, unlike some of the transition elements, these elements (apart from Zn, Cd, Ga and Tl(I)) do not form isolable tetrahydroborates.[216] The discovery that stannous chloride gives diborane in yields of up to 94% on heating to *c.* 200°C with $NaBH_4$ in the absence of a solvent[261–2] was promising. Some higher boranes are produced simultaneously. Unfortunately a little stannane SnH_4 is also formed, and this compound is troublesome to remove. Similar reactions have been effected in diglyme solution by the chlorides of bismuth and tin(IV), with reported yields of 38 and 65%.[263]

In diglyme no higher boranes are produced. Recent studies of the action of various metal halides with $LiBH_4$ and $NaBH_4$ in diglyme have shown that yields of 98% may be obtained with the chlorides of antimony(III) and mercury(I) at the ambient temperature.[264] A disadvantage of antimony halides (comparable with that of the tin halides) is that traces of stibine SbH_3 appear. However, mercury halides suffer from no such drawback and give a very pure product in 98% yield on freezing it out from the hydrogen released:

$$2NaBH_4+Hg_2Cl_2 \xrightarrow{\text{diglyme}} B_2H_6+H_2+2NaCl+2Hg$$

The mercury and the solvent are recoverable. This then is perhaps the most convenient method, since it avoids the use of gases, more volatile ethers or external heating, and gives a high yield. Moreover, the product is free from BF_3, which is especially important if the diborane(6) is required for selective reductions.[222] Alternatively a 98% yield may also be obtained with iodine[264]:

$$2NaBH_4+I_2 \xrightarrow{\text{diglyme}} B_2H_6+H_2+2NaI$$

In the latter case, interaction with the solvent needs to be prevented by keeping the concentration of I_2 low and by removing the diborane from the solution as soon as it is formed. This is realized by working with an evacuated system. The iodine and the solvent may be recovered.

FROM COVALENT COMPOUNDS CONTAINING BORON-HYDROGEN BONDS

Compounds that contain the BH_3, BH_2 or BH grouping can frequently be made to liberate diborane. Thus many compounds of borane with donors, e.g. ethylenediamine bis-borane $(CH_2NH_2BH_3)_2$[265], yield diborane with substances such as $BF_3.Et_2O$ in a displacement reaction:

$$(CH_2NH_2BH_3)_2+2BF_3.Et_2O \rightarrow B_2H_6+(CH_2NH_2BF_3)_2+2Et_2O$$

With BCl_3 such reactions are likely to be less simple[266] and the yield correspondingly lower. In other cases simple dissociation occurs, e.g.[267–8]

$$2BH_3CO \rightleftharpoons B_2H_6+2CO$$

$$2BH_3PF_3 \rightleftharpoons B_2H_6+2PF_3$$

(though the reaction mechanisms are less simple than indicated by the equilibrium equations); or diborane is released by disproportionation[269–72]:

$$6B_2H_5Cl \rightleftharpoons 5B_2H_6+2BCl_3$$

$$6B_2H_{6-n}Me_n \rightleftharpoons (6\text{–}n)B_2H_6+2nBMe_3$$

$$6BH(OMe)_2 \rightleftharpoons B_2H_6+4B(OMe)_3$$

In such cases it is usually necessary to remove the diborane progressively as it is formed. These reactions are generally of little practical use, since the starting material frequently requires diborane for its preparation. Dimethoxyborane is however an exception, and one production method makes use of its disproportionation[273] at the top of a reflux column.

It has been known for a long time[1] that diborane is one of the major products of the thermal decomposition of tetraborane(10) at about 100°C. The addition of hydrogen may improve the yield, partly because it suppresses the pyrolysis of the diborane formed.[161] Diborane is also readily liberated from B_4H_{10} by the action of certain Lewis bases[274–5] and (together with ethyldiboranes) from B_5H_{11} by the action of ethylene.[276] Lewis-base adducts of triborane(7) such as $Me_2O.B_3H_7$ break down, even at room temperature, to give a mixture of B_2H_6 and higher boranes.[275, 277] In the pyrolysis of hydrogen-rich boranes about 50% of the boron terminates in an unwanted, yellow non-volatile solid boron hydride. However, if has more recently been found that part of the diborane can be recovered on heating the solid hydride to 800°C or above in hydrogen.[278] Hydrogen-poor boranes give little or no B_2H_6 on pyrolysis.

FROM REDUCTION BY MEANS OF METAL ALUMINIUM HYDRIDES

Apart from those described above, all chemical methods of preparing diborane must of necessity involve reduction with hydrogen-containing materials, and since the complex metal aluminium hydrides are in general the most effective examples in laboratory use, preparations using these compounds deserve separate consideration.

The source of the boron is conveniently a boron halide or an ester of boric acid. Initial experiments involved the reaction of boron trichloride with lithium aluminium hydride in ether solution at low temperatures (at which, apparently, the ether is not appreciably cleaved by the boron trichloride) to give a reported yield of 99·4%.[279] Historically this is important as the first reaction discovered to give an essentially quantitative yield of diborane:

$$3LiAlH_4+4BCl_3 \rightarrow 2B_2H_6+3(LiCl+AlCl_3)$$

Instead of BCl_3, boron trifluoride etherate has been used[114], but it was later shown[280] that this reaction (now often referred to as Shapiro's method) proceeds well short of quantitatively and is complex, taking place in at least two principal stages; thus very little B_2H_6 is evolved until 75% of the theoretical amount of the $BF_3.OEt_2$ has been added. This suggests that the first stage is the formation of $LiBH_4$:

$$LiAlH_4 + BF_3.OEt_2 \xrightarrow{Et_2O} LiBH_4 + AlF_3 + Et_2O$$
$$3LiBH_4 + BF_3.OEt_2 \longrightarrow 2B_2H_6 + 3LiF + Et_2O$$

The first stage of the reaction is more vigorous than the second, which has already been discussed on p. 71. Yields are in the range 85–90%. If the $LiAlH_4$ solution is added to the $BF_3.OEt_2$ the liberation of diborane commences at the outset, but the yields are still further reduced. Lithium tetrafluoroborate and at least one lithium aluminium fluoride were shown to be produced (in addition to AlF_3); but the non-quantitative yields of B_2H_6 by Shapiro's method[280] cannot be explained by $LiBF_4$ formation, since this substance was shown in a separate experiment to give diborane with $LiAlH_4$ in ether solution (albeit in only about 60% yield):

$$3LiAlH_4 + 4LiBF_4 \rightarrow 2B_2H_6 + (7LiF + 3AlF_3)$$

Caution is recommended, since failure to adhere rigidly to Shapiro's instructions has on occasion led to explosion, apparently through the accumulation of peroxide compounds in the $BF_3.OEt_2$[281–2], which should always be purified by distillation prior to use.

The corresponding reactions with $NaAlH_4$ in a suitable solvent in place of $LiAlH_4$ in ether have been studied. The reaction of $NaAlH_4$ with BF_3 or $BF_3.OEt_2$[283] is somewhat complex and $NaBH_4$ formation occurs unless it is carried out at a higher temperature. In diglyme a fair yield of B_2H_6 is obtained at 80°–100°C. The addition of $AlCl_3$ improves the yield, which may become quantitative.[284] The reaction of $NaAlH_4$ with BCl_3 gives a product contaminated with chloroboranes unless ether is present, when the adduct $AlCl_2BH_4.OEt_2$ is an isolable intermediate.[285] In tetrahydrofuran or heptane-diglyme mixtures BCl_3 gives fair yields and, as might be expected, the reaction proceeds in stages with $NaBH_4$ appearing at an intermediate stage.[284] As an alternative to $NaAlH_4$, the calcium salt $Ca(AlH_4)_2$ will reduce boron halides to diborane in dioxane solution.[286]

In ether or diglyme, triphenyl borate, but not trimethyl borate, produces diborane with either $LiAlH_4$ or $NaAlH_4$, though in restricted yield.[239, 287] In this case it is essential to add a solution of the aluminium compound to the ester, for no diborane results if the order of addition is reversed. A disadvantage of this reaction is that the metal tetrahydroborate and possibly the heptahydrodiborate occur as by-products.

FROM REDUCTION BY MEANS OF SIMPLE HYDRIDES AND THEIR DERIVATIVES

An early set of experiments with hydrides was complicated by the fact that hydrogen was admixed with the boron halides before these were passed through the reduction chamber.[288] In general, the simple metal hydrides are less reactive towards boron halides than the complex aluminium hydrides. Thus lithium hydride LiH gives very little, if any, diborane on direct interaction with, for example, BF_3 or BBr_3 at temperatures as high as 180°C.[289] It has, however recently been claimed that at still higher temperatures, e.g. 390°–430°C, diborane can be produced by the direct method provided it is removed from the heated zone as soon as it is formed.[290] With boron trifluoride etherate in excess ether, however, an exothermic reaction commences at room temperature, and diborane is evolved in good yield:

$$6LiH + 8BF_3.OEt_2 \xrightarrow{Et_2O} B_2H_6 + 6LiBF_4 + 8Et_2O$$

Although this observation was not published in the open literature until 1953[289], it had in fact been mentioned in an unpublished report dated 1943, and this interval provided certain American workers with the opportunity for further study and improvements in the meantime. Thus it was reported in 1952[220] that the addition of small quantities of ether-soluble promoters containing active hydrogen, e.g. $LiBH_4$ or $LiBH(OMe)_3$, causes the reaction to take a different course and proceed in two stages via $LiBH_4$ as an intermediate:

$$12LiH + 3BF_3.OEt_2 \xrightarrow[Et_2O]{promoter} 3LiBH_4 + 9LiF + 3Et_2O$$

This results in a considerable saving of boron trifluoride, since, as mentioned above, $LiBH_4$ reacts further to give not $LiBF_4$, but LiF, so that the overall reaction now becomes

$$6LiH + 2BF_3.OEt_2 \xrightarrow[Et_2O]{promoter} B_2H_6 + 6LiF + 2Et_2O$$

All the exothermicity is however associated with the first stage, and the diborane is only released during the second stage after 75% of the $BF_3.OEt_2$ has been added.

In the absence of promoter, the last reaction can also be realized by the application of pressure[220], this hindering the escape of the B_2H_6 and favouring reaction with further LiH to form $LiBH_4$, which, once formed, is self-promoting. In tetrahydrofuran the same occurs without the application of pressure, possibly because diborane is much more soluble in this solvent than in ether and is thus afforded greater opportunity to react with the lithium hydride. Even in diethyl ether, if the reactants are kept to within a few degrees of 0°C by external cooling, the latter course can be made to predominate. Under such conditions, an interesting feature may be the appearance of what has been referred to as a 'surge' reaction. Part or all of the boron trifluoride etherate can be added and the mixture allowed to stand, but no diborane is evolved below 5°C, even after several hours. At the end of this time it may be possible to show that some solid $LiBH_4$ has separated. If now the cooling bath is removed and the reaction vessel allowed to warm up, the temperature suddenly rises and the diborane is evolved in a sudden surge while the ether boils.[220] No explanation was suggested for this when the observation was first made, but it is possible that the phenomenon is due to the presence in solution of an unstable and endothermic complex between diborane and dissolved $LiBH_4$. Russian workers have shown that these reactants give the best yields of diborane in the temperature range 10°–25°C[291] and that the reaction is activated by bromine or iodine.[292] As a consequence solvents such as benzene can be used at 35°C. Best yields are obtained if an excess of the boron trifluoride etherate is used.

Lithium hydride does not react with $LiBF_4$ suspended in ether to give appreciable quantities of diborane unless the reaction is promoted, e.g. with $LiBH_4$ or $B(OMe)_3$.[220] The action of the last-named compound is probably first to form $LiBH(OMe)_3$.

Because the complex salt $LiBCl_4$ has no stable existence, the reaction between LiH and BCl_3 would be expected to be analogous to the foregoing two-stage process. This is borne out by experiment.[220] The reaction is exothermic with diborane yields of 70–77%. A much purer product is obtained by the use of BCl_3 rather than its etherate, presumably because ether-cleavage is thereby minimized.[293] A modification of this reaction involves the recycling of part of the diborane, which is made to react with the LiH in an ether slurry to give $LiBH_4$, and this in turn is treated in a separate vessel with BCl_3 under pressure to give diborane in high yield.[294] This procedure presents some advantage over the use of $BF_3.OEt_2$, because the lithium is more easily recovered when the by-product is LiCl rather than LiF.

It would be a great advantage if the less expensive sodium hydride reacted as readily as the lithium compound, but unfortunately it does not do so. This lack of reactivity is probably in part associated with the much lower solubility of sodium compounds in organic solvents, so that the NaH becomes coated with products such as $NaBF_4$ or NaF and is largely inactivated. Thus yields of only 30–60% of diborane are obtained with $BF_3.OEt_2$ unless the NaH is exceptionally finely ground or the reaction is carried out in a vessel in which continuous mechanical grinding is maintained, e.g. by means of steel balls.[289] Alternatively the NaH may first be converted by means of trimethyl borate to $NaBH(OMe)_3$, which in ether reacts smoothly with $BF_3.OEt_2$ to give diborane; but the yields based on active hydrogen are only good if the boron compound is present in 100% excess, which presumably prevents loss through the formation of dimethoxyborane $BH(OMe)_2$, a relatively stable substance which only slowly disproportionates to diborane and trimethyl borate.

In diglyme or polyglymes, NaH may be used directly with BF_3 and is converted almost quantitatively to diborane, provided only that a large excess of BF_3 is used.[234, 295] The excess is essential to prevent the retention of diborane in solution as NaB_2H_7.

Moreover the solid residue is unfortunately $NaBF_4$ and not NaF. Sodium hydride will also reduce trialkoxyboroxines to diborane.[296]

Both MgH_2 and CaH_2 have been suggested as alternatives to NaH for reducing BCl_3 to diborane.[297] They can be used suspended with an aluminium halide in either benzene or an alkylated benzene. Alternatively MgH_2 can also serve as the active agent in a cyclic process involving H_2.[298] In the absence of a solvent, calcium hydride will react with gaseous BF_3 at 225°C according to the equation

$$3CaH_2 + 2BF_3 \rightarrow B_2H_6 + 3CaF_2$$

but the yield is poor.[299] With respect to hydridic hydrogen the yields are somewhat better if the reaction is carried out in solution, but $Ca(BF_4)_2$ instead of CaF_2 is then the solid residue, so that the conversion with respect to BF_3 is reduced. Suitable solvents are diglyme[259] and tetrahydrofuran[300], and in these the temperature required is reduced to < 100° and *c.* 140°C respectively. Calcium hydride also reacts with $BF_3.OEt_2$ at 120°C, but a large excess of the latter is required to avoid complications and to give a good yield of diborane.[301] The reaction with boron trichloride is unsatisfactory. Even in solution it is sluggish, so that little diborane is formed; moreover, cleavage of the solvent may be severe, as in the case of monoglyme.[259] It must therefore be concluded that CaH_2 is very much less reactive than LiH or NaH for this purpose, and, in the absence of experimental evidence, the same would be expected of SrH_2 and BaH_2.

The simple hydrides of the group-III metals have not been extensively studied with respect to their ability to reduce boron compounds to diborane, but there is a reference[211] to an industrial report which records that aluminium hydride is effective. It thus converts triphenyl borate to diborane.[302] Similarly its dialkoxy derivatives of formula $AlH(OR)_2$ are also known to reduce boron halides to the same compound.[303]

Of the hydrides of the non-metals, only those of silicon and carbon have so far been reported to produce diborane, but even with these the position is a little complex. Thus BCl_3 exchanges halogen for hydrogen quantitatively with disilane Si_2H_6 at 0°C[304], but not at all with SiH_4 or SiH_3Cl; nor will BF_3 exchange with Si_2H_6. Failure to react is probably not attributable to thermodynamic factors in any of these cases, but may be linked with inability of the mixtures to initiate a suitable chain reaction, since BCl_3 and SiH_4 will give diborane in the presence of methyl radicals[305], or if they are heated in a sealed vessel at 150°–155°C.[306] There is good evidence that the first product is dichloroborane $HBCl_2$, which subsequently disproportionates to diborane.

$$BCl_3 \xrightarrow[155°C]{SiH_4} HBCl_2 \rightleftharpoons \tfrac{1}{6}\,B_2H_6 + \tfrac{2}{3}\,BCl_3$$

At least one partially substituted organosilane will give diborane with BCl_3.[307] Alternatively, CH_4 will undergo essentially the same reaction as SiH_4, but the temperature required is 750°–800°C, whereas other alkanes react at slightly lower temperatures.[308] Some success has been achieved with certain other organic compounds at still lower temperatures, for example by decomposing aldehydes and ketones admixed with BCl_3 or BBr_3 in the presence of various catalysts. A conversion to diborane of 70% is claimed for mixtures of the tribromide and formaldehyde when passed over a catalyst of copper on kieselguhr at 400°C.[309]

Hydrogen sulphide will react with boron tribromide, but not to give B_2H_6 directly. The first product is the cyclic compound $B_3S_3(SH)_3$, which only gives diborane on hydrogenation.[310]

FROM REDUCTION BY MEANS OF ELEMENTAL HYDROGEN

Many attempts have been made to discover an efficient and practical method for preparing diborane by the direct action of gaseous hydrogen, since this would have certain advantages for large-scale production. Although definite advances have been made, it is however debatable whether the advantages are not more than offset by disadvantages inherent in each method proposed to date.

Since diborane is an endothermic compound, it could not be expected to be formed in quantity by direct interaction of the elements, other than possibly by the electrolytic means discussed below. Whether any is formed at all by ordinary chemical means depends upon the boron used. Thus negative results were obtained with boron prepared from borax and aluminium, but traces were shown to be formed from a commercial sample of boron of purity 96·9% and hydrogen at 840°C.[311] It may therefore be suspected that impurities such as metal borides play a role. Atomic hydrogen has also been suggested[312] and tried[313], but with boron of high purity it produced only a trivial amount of diborane. However, boron in a suitable form, when admixed with a metal oxide such as MgO[314] or with a metal sulphide such as Cu_2S[315], reacts to give diborane when heated strongly in a stream of hydrogen.

The reaction of hydrogen with borides has been little studied. Evidence of diborane formation has been found at *c.* 400°C with the borides of magnesium, calcium and nickel, and at 250°C with that of zinc.[311] No or very little reaction occurs, however, with the refractory borides of transition metals, even at very high temperatures.[316]

The replacement of halogen in BCl_3 or BBr_3 by hydrogen is a particularly interesting type of reaction. Its feasibility was first demonstrated in 1931 in a method involving the passage of an electric discharge through a mixture of hydrogen and boron trichloride vapour.[270] Provided the concentration of BCl_3 vapour was high enough, a moderate yield of diborane was observed to be formed directly, while further quantities could be obtained by progressive disproportionation of the main product, a chloroborane which was originally assumed to be B_2H_5Cl:

$$2BCl_3+5H_2 \xrightarrow[\text{discharge}]{\text{electric}} B_2H_5Cl+5HCl$$

$$6B_2H_5Cl \rightleftharpoons 5B_2H_6+2BCl_3$$

But in the light of more recent studies on the interaction of BCl_3 with B_2H_6[317], it is hard to believe that the intermediate chloroborane—at least in the initial stages—was not the then unknown $HBCl_2$; this compound has a volatility rather similar to that of B_2H_5Cl and disproportionates into the same products. Accordingly the principal steps of the original reaction mechanism[318], also cited later[211], may more plausibly be written:

$$BCl_3 \xrightarrow{\text{electric discharge}} BCl_2+Cl$$

$$H_2 \xrightarrow{\text{electric discharge}} H+H$$

$$BCl_2+H \rightarrow HBCl_2$$

$$(\text{or } 2BCl_2 \rightarrow B_2Cl_4 \xrightarrow{H_2} 2HBCl_2)$$

$$5HBCl_2 \rightleftharpoons B_2H_5Cl+3BCl_3$$

$$\text{or } 6HBCl_3 \rightleftharpoons B_2H_6+4BCl_3$$

Though still slow by modern standards, at the time of its discovery this method greatly facilitated the laboratory preparation of diborane. Earlier workers had relied on the rather tortuous and wasteful—if historically important—procedure due to Stock, which involved the pyrolysis of higher boranes obtained from magnesium boride[81, 319–20], itself only obtainable from a high-temperature fusion process.[321]

Heating hydrogen with BCl_3 or BBr_3 will also give diborane, but high temperatures (550°–950°C) are required.[322] More recent improvements of the method involve passing the reactants at 650°C through a bed containing a catalyst, which may be either activated carbon[323], or metallic copper or silver[324]; or, alternatively, the catalyst may be a more active metal such as iron, magnesium, zinc, aluminium or an alkali or alkaline earth metal, for which a lower temperature in the neighbourhood of 350°C suffices.[288, 325] With aluminium in a fluidized bed, yields approaching 34% have been reported.[326] Even the much less active boron and boron carbide will serve, but much higher temperatures are required.[327] Or again, the boron trichloride may be converted to its trimethylamine adduct and subjected to prolonged heating with H_2 at 200°C and

2,000 atm; the diborane is subsequently liberated by more halide, which simultaneously reforms the original adduct[328]:

$$Me_3N.BCl_3 \xrightarrow[\text{200°C, pressure}]{H_2} Me_3N.BH_3 \xrightarrow{BCl_3} \tfrac{1}{2}B_2H_6 + Me_3N.BCl_3$$

Alkyldichloroboranes $RBCl_2$ are easier to convert than BCl_3, and will give yields of up to 50% of B_2H_6 at 320°–340°C with H_2 under pressure over activated carbon.[329] The reaction proceeds via $HBCl_2$.

Trialkylboranes also undergo a thermodynamically favourable reaction with hydrogen, and yields approaching 75% are obtained at 150°–200°C and 100–130 atm[330]

$$2BR_3 + 6H_2 \xrightarrow[\text{100 atm}]{\text{200°C}} B_2H_6 + 6RH$$

Again, a like reduction will take place, preferably at pressures of about 350 atm, if the trialkyl is in the form of its trimethylamine adduct, and this is the essential step in a recently patented multistage process in which the raw materials are $B(OR)_3$, $AlEt_3$, NMe_3, H_2 and $BF_3.OEt_2$.[331] Esters such as $B(OMe)_3$ may, however be reduced in a single-stage operation with H_2 (e.g. at 170°C and 800 atm) in the presence of an electropositive metal such as aluminium and a halide flux that is inert towards diborane(6).[332]

The cheapness and availability of boric oxide have resulted in many attempts to reduce it directly. This is a difficult operation, but it is of particular interest to note that the preceding reaction will proceed (with or without a catalyst) when B_2O_3 is used as the raw material in place of $B(OR)_3$.[333–5] There are reasons for believing that this reaction may proceed via aluminium chlorohydride as intermediate arising from partial reduction of the $AlCl_3$ in the flux. An alternative procedure is the reduction of boric oxide or a metal borate in two stages, in the first to the monoxide BO by firing it with boron[336], carbon[337] or boron carbide B_4C.[337] The monoxide is then reduced to B_2H_6 in a stream of hydrogen at a temperature in the range 1,000°–1,300°C, depending upon the method adopted for the first stage. The reaction can be carried out in a single stage[338], but in the presence of carbon the diborane produced is contaminated with borane carbonyl.

FROM REDUCTION BY ELECTROLYTIC MEANS

Although, as seen on p. 71, it is relatively easy to electrolyze metal tetrahydroborates[245–6], a suitable electrolyte for the electrolytic reduction of elementary boron at ordinary temperatures has not been reported. At elevated temperatures, however, melts of metal halide mixtures that liquefy <400°C are serviceable; one example consists largely of LiCl and KCl. If a fine stream of dry oxygen-free hydrogen is passed through this melt while it is subjected to electrolysis, diborane admixed with higher boranes is evolved at a boron anode.[339] A disadvantage of the method is the necessity to replace the anodes periodically. An alternative is to use metal electrodes and introduce BCl_3 while the cathode is kept flushed with hydrogen.[340] Under these conditions lithium hydride instead of lithium is then formed continuously at the cathode and reacts with the boron trichloride to give boranes. A disadvantage of this method is the need to separate the product from chloroboranes and unreacted BCl_3.

Fragmentation by Physical Means

The fragmentation of diborane(6) leads to immediate and irreversible decomposition, as could be predicted from the endothermicity of this compound. Except under the most severe conditions, however, elemental boron is not normally a major product. The physical methods that have been used to fragment B_2H_6 are pyrolysis, ultrasonic shock waves, photolysis, irradiation with γ rays, electron impact, positive-ion impact, and the electric discharge. The behaviour of B_2H_6 when subjected to physical fragmentation is summarized in Table XI.

Table XI.—Summary of Behaviour of Diborane(6) on Subjection to Fragmentation by Physical Means

Method	Initial reaction	Identified product species	Intermediates(a)	Ref.
Pyrolysis	$2B_2H_6 \rightarrow B_3H_9 + BH_3$(b)	H_2, B_4H_{10}, B_5H_{11}, B_5H_9, B_6H_{10}, $B_{10}H_{14}$, $(BH)_x$. Proportions depend on conditions	BH_3, B_3H_9, B_3H_7, B_4H_8, B_6H_{12}, n-B_9H_{15}, B_8H_{12}, B_9H_{13}	81, 341–352, 17, 18
Shock wave		Similar to those from pyrolysis	BH_3, B_3H_9, B_3H_7, B_4H_8, B_6H_{12}, (B_7H_{11} ?), (B_7H_{13} ?)	353, 354
Photolysis: (i) low intensity;	$B_2H_6 \xrightarrow{h\nu} B_2H_5 + H$ ($B_2H_6 \xrightarrow{h\nu} B_2H_4 + H_2$?)	H_2, B_4H_{10}, B_5H_{11}, $(BH)_x$	B_2H_5, (B_2H_4 ?)	68, 69, 355, 356
(ii) flash		BH		357, 358
Gamma radiation	$B_2H_6 \rightarrow B_2H_5 + H$	B_4H_{10}, traces of higher boranes	B_2H_5	359, 70
Electron impact		$B_2H_6^+$, $B_2H_5^+$, $B_2H_4^+$, $B_2H_3^+$, $B_2H_2^+$, B_2H^+, B_2^+, BH_3^+, BH_2^+, BH^+, B^+, $B_2H_x^{2+}$, $B_2H_5^-$, $B_2H_4^-$, $B_2H_3^-$, $B_2H_2^-$, B_2H^-, B_2^-, BH_4^-, BH_3^-, BH_2^-, BH^-, B^-, heavier species (e.g. $B_3H_5^+$, $B_4H_4^+$, $B_2H_7^-$) from secondary processes		145, 8, 352, 27, 160, 23, 16, 80
Positive-ion impact		BH_4^-, $B_2H_7^-$, $B_2H_5^-$, $B_3H_8^-$, $B_3H_7^-$, $B_4H_9^-$, $B_4H_8^-$, $B_5H_{10}^-$ (and possibly BH_3^-, $B_2H_3^-$, $B_3H_6^-$, $B_3H_9^-$, $B_3H_{10}^-$) $B_4H_7^-$, $B_4H_{10}^-$, $B_4H_{11}^-$		360
Electric discharge: (i) spark;		H_2, solid $BH_{0\cdot 4}$		361
(ii) silent		H_2, B_4H_{10}, B_5H_{11}, B_5H_9, B_6H_{10}, n-B_9H_{15}, $B_{10}H_{14}$, (B_6H_{12} ?), (B_7H_{17} ?), B_8H_{12}, $B_{10}H_{16}$, $B_{20}H_{16}$, $(BH)_x$		361–369, 19

(a) Not always positively identified, and in some cases tentatively proposed in inference.

(b) See text pp. 80, 135.

PYROLYSIS

As has long been known[81], the principal products from the pyrolysis of diborane(6) at moderate temperatures are H_2, B_4H_{10}, B_5H_9, B_5H_{11}, $B_{10}H_{14}$ and a non-volatile solid hydride of composition $(BH)_x$. Small quantities of B_6H_{10} are sometimes observed, and there are good reasons for believing that traces of other species are present in pyrolyzing diborane(6). Thermal decomposition of B_2H_6 is already noticeable below 100°C—indeed, even at room temperature upon storage for a matter of months—and becomes rapid in the temperature range 150°–200°C, being about five times as fast for B_2H_6 as for B_2D_6.[341]

The relative proportions of the products are markedly dependent on the conditions.[81, 342–52, 17, 18] The modification of the conditions for the purpose of favouring the formation of selected products is discussed on p. 83. Notwithstanding the endothermic nature of the compound, elemental boron is not formed unless sufficiently high temperatures are used: a temperature of 700°–800°C is adequate for decomposing B_2H_6 quantitatively into boron and hydrogen.[319]

The effects of solid catalysts such as activated Al_2O_3 and metallic nickel or platinum on the thermal cracking of B_2H_6 have been examined[370–1], but although some activity was noted, no conclusive evidence for directional catalysis was found, and in general the effectiveness of solid catalysts is severely restricted because they rapidly become coated with solid degradation products.

As discussed on p. 135, the initial act in the pyrolysis is not ordinarily unimolecular dissociation, but one which nevertheless produces free molecules of BH_3 by the energetically more favourable bimolecular step $2B_2H_6 \rightarrow B_3H_9 + BH_3$. This species very rapidly reacts further, so that a directly observable concentration is not permitted to accumulate. Traditionally, BH_3 production by symmetric fission has been regarded as reasonable, since the bridge bond is probably the weakest bond in B_2H_6, and is the only one likely to have a sufficiently low dissociation energy to account for the observed decomposition of diborane at 100°C and below; but the mass of accumulated evidence now indicates[18] that unimolecular symmetric fission only becomes significant as an inefficient process under extreme conditions of low pressure and high temperature. It has however been claimed[158, 372] that mass-spectroscopic evidence from electron-impact studies in low-pressure, high-temperature pyrolyses indicates that the asymmetric fission

$$\begin{aligned} B_2H_6 &\rightarrow BH_2 + BH_4 \\ &\rightarrow 2BH_2 + H_2 \end{aligned}$$

is the more important. Such a method of fragmentation would be surprising for energetic reasons. In similar mass-spectroscopic studies with isotopic species, other workers[160] have confirmed the appearance of the positive ion BH_2^+, but found no evidence in the face of a high appearance potential to support the supposition that this ion arises from the neutral radical BH_2 rather than from the molecule BH_3. Independent confirmation that the appearance potential of the ion BH_2^+ is higher than that of BH_3^+ has been forthcoming[74, 170] and would appear to dispense with the possibility that appreciable quantities of the BH_2 radical are formed, since this would give rise to the ion BH_2^+ at a lower appearance potential. Indeed, the above mechanism proposed on the basis of the active participation of the BH_2 radical has now been withdrawn as far as the pyrolysis system is concerned.[27] It does not follow that this mode of initial decomposition is also absent in other fragmentation processes such as photolysis, however.

SHOCK WAVES

Apparently only two studies of the behaviour of diborane in the shock tube have been made. Open reference has been made to an unpublished report[353], in which it is claimed that the production of free BH_3 was detected by means of mass spectrometry. The other study[354] discloses evidence for the subsequent formation of heavier unstable intermediates without revealing the identity of the primary fragments.

PHOTOLYSIS

It was initially observed by Stock[81] that irradiation of diborane(6) with ultraviolet light causes an increase in volume and the deposition of a yellowish-white crystalline solid. More recently, in both the monochromatic photolysis by ultraviolet radiation of wavelength 1849 Å[68–9] and the mercury-photosentized decomposition[355], photodissociation of B_2H_6 to $B_2H_5 + H$ is assumed to be the major primary step, because the principal products are H_2 and B_4H_{10}.

Whether this is accompanied to some extent by a competing primary photodissociation to $B_2H_4+H_2$, is not yet certain. The evidence for it is compatible with experiment, but not compelling. The formation of B_2H_4 is also assumed in the hexafluoroacetone-sensitized photolysis[356], but here the B_2H_4 is supposed to arise from the condensation of two BH_2 radicals produced from asymmetric fission of B_2H_6 as the primary step. In the straight photolysis the simultaneous formation of B_5H_{11} has been taken to indicate a competing dissociation of B_2H_6 to $2BH_3$ (with no significant recombination)[68], whereas B_5H_9 and only a little B_5H_{11} appeared as additional products in the mercury-sensitized decomposition.

Clearly the mechanism in photolysis differs from that in pyrolysis, and this will rest not only on a possible difference in the initial step and excess kinetic energy of the fragments, but also on the fact that these experiments were carried out at temperatures at which interconversion of B_4H_{10} and B_5H_{11} is insignificant. It must, however be stated that the mechanisms proposed[355, 68–9] to explain the formation of B_4H_{10} from $2B_2H_5$ are not entirely satisfactory, in that they do not account adequately for certain features connected with the observed amount of hydrogen formed and the quantum yields.

In flash-photolysis experiments with B_2H_6[357–8], both on its own and admixed with oxygen, the only fragment detectable by its spectrum was BH. Although this spectrum[373–4] and that of BH_2[375] (which is bent—angle 131°—in its ground state) were produced in the flash photolysis of borane(3) carbonyl $BH_3.CO$, again no spectrum due to BH_3 was observed. Indeed, the spectrum of BH_3 in the gas phase (as distinct from a solid matrix at low temperatures) has never been observed, and lines once attributed to this species almost certainly belong to other unstable intermediates such as B_3H_9, B_3H_7 or B_4H_8.

IRRADIATION WITH γ RAYS

As could be expected, the principal product of decomposition of diborane(6) with γ radiation from ^{60}Co as source[359] is the same as with ultraviolet light. At a few percent decomposition, tetraborane(10) B_4H_{10} and only traces of higher boranes are obtained. That B_2H_5 radicals are initially formed, has been demonstrated by e.s.r. studies.[70]

ELECTRON IMPACT

Early electron-impact experiments with diborane[145, 8] produced evidence for the formation of the complete series of singly charged ions, $B_2H_6^+$, $B_2H_5^+$, $B_2H_4^+$, $B_2H_3^+$, $B_2H_2^+$, B_2H^+, B_2^+, BH_3^+, BH_2^+, BH^+ and B^+, and for certain doubly charged ions. However, the peaks for $B_2H_6^+$ and BH_3^+ are either extremely weak or are not observed at all, so that there remained at least a suspicion that they might be due to N_2^+ and N^+ or to organic fragments in the background; moreover, initial studies with $^{10}B_2H_6$[8] of isotopic purity 96% hardly cleared up this matter, particularly in the case of $B_2H_6^+$. But the existence of both ionic species, which appeared probable from studies with deuterodiborane(6) B_2D_6[14], was put beyond reasonable doubt by the values obtained for the appearance potentials of $B_2H_6^+$ and BH_3^+.[376] The original claim that these are indistinguishable at $12{\cdot}1 \pm 0{\cdot}2$ eV would imply that the dissociation process

$$B_2H_6^+ \rightarrow BH_3 + BH_3^+$$

requires very little energy, but other workers[377, 74] have since found wide differences for these appearance potentials, indicating that a relatively large amount of energy is absorbed in the dissociation of the bridge bond of $B_2H_6^+$.

Under pyrolyzing conditions the BH_x^+ ions may also be obtained from monomeric BH_3, as has been demonstrated[158, 160, 74], but the possibility that some might also arise through the presence of neutral BH_2 seems to have been refuted (see p. 80). By virtue of careful work, it has been possible to distinguish between BH_3^+ produced from BH_3 and that produced from B_2H_6; and indeed, the appearance potentials of the two processes producing BH_3^+ are markedly different, namely $12{\cdot}32 \pm 0{\cdot}1$ and $14{\cdot}88 \pm 0{\cdot}05$ eV respectively.[74] It has also been possible to confirm the existence of $B_2H_6^+$ and to argue rather convincingly that the electron lost is from a terminal bond, since the dissociation energy $D(BH_3^+—BH_3)$ is actually greater than $D(BH_3—BH_3)$.[74] This conclusion has since found support from the results of photoelectron spectroscopy.[142–3, 128] However, the dissociation energies from the electron-impact work include any potential barriers to be overcome, and because the species BH_3 (unlike the radical CH_3) has no unpaired electron, these could be considerable.[18] For other pyrolyzing conditions indirect evidence has been obtained for the presence of higher unstable intermediates[352, 27, 160] (apart from isolable boranes), including a triborane and a new tetraborane species, B_4H_8.

Negative ions have also been produced from diborane. Although the earliest attempt[378] in this direction failed, more recently[23, 16] the ions $B_2H_5^-$, $B_2H_4^-$, $B_2H_3^-$, $B_2H_2^-$, B_2H^-, B_2^-, BH_4^-, BH_3^-, BH_2^-, BH^- and B^- have been detected, but not $B_2H_6^-$. The ion $B_2H_7^-$ can arise from the secondary process

$$BH_4^- + B_2H_6 \rightarrow BH_3 + B_2H_7^-$$

as shown by ion cyclotron resonance.[80]

POSITIVE-ION IMPACT

The newer technique of positive-ion impact for producing negative, as well as positive, ions has already proved decidedly fruitful when applied to diborane(6). The method involves bombarding the molecules of a gas with positive ions from an accelerator, thus subjecting the molecules to much heavier impacts than are usual in electron-impact work. The negative ions produced are then collected with high efficiency and deflected into a beam for analysis in a mass spectrometer. By means of this method, which had previously been employed for producing negative ions from H_2O, NH_3 and BF_3 molecules[379], B_2H_6 of various isotopic compositions was bombarded with krypton ions of energy 30 keV and evidence obtained for the formation of the negative ions BH_3^-, BH_4^-, $B_2H_3^-$, $B_2H_5^-$, $B_2H_7^-$, $B_3H_6^-$, $B_3H_7^-$, $B_3H_8^-$, $B_3H_9^-$, $B_3H_{10}^-$, $B_4H_7^-$, $B_4H_8^-$, $B_4H_9^-$, $B_4H_{10}^-$, $B_4H_{11}^-$ and $B_5H_{10}^-$, although admittedly only about half of these were positively identified.[360] It is to be hoped that further studies of this type will be made, especially since positive ions of one or more than one unit charge are also produced by this process.[379] But no studies have yet been carried out on the positive ions produced in this way from B_2H_6.

THE ELECTRIC DISCHARGE

On subjecting diborane(6) at 10–15 Torr pressure to a high-density electric discharge, it was observed that rapid and quantitative decomposition occurred and resulted in the formation of a uniform brown solid of approximate composition $BH_{0.4}$ that probably contained elemental boron.[361]

In contrast, a silent electric discharge in an ozonizer produced a highly reactive greenish-yellow solid of formula $(BH)_x$ as a transparent film together with a mixture of B_5H_{11} and B_5H_9. The reaction was accompanied by the appearance of a reddish-blue glow discharge. Under controlled conditions the principal product is tetraborane(10) B_4H_{10}[362–3], but under other conditions a whole spectrum of higher hydrides is produced.[364] In one attempt to isolate less common or unknown boranes from such mixtures[365], octaborane(12) B_8H_{12} was obtained along with mass-spectral evidence for B_9H_{15} and the unknown borane B_7H_{17}. However, experimental confirmation is lacking and it has been suggested that the supposed existence of B_7H_{17} and the supposed production of B_6H_{12} by this method[366] are based on a misinterpretation of the evidence.[367] On the other hand, the higher boranes B_8H_{12}[19], $B_{10}H_{16}$[368] and $B_{20}H_{16}$[369] have definitely been isolated from the products obtained by the use of the electric discharge.

As yet, very little has been done concerning the discharge-induced fragmentation of diborane in the presence of other substances. This procedure constitutes an interesting development and promises to provide a way of producing unusual or hitherto unknown borane derivatives. Thus, in a glow discharge, diborane(6) admixed with oxygen will give the species $H_2B_2O_3$ and $H_3B_3O_3$[380], whereas admixed with acetylene it produces a mixture of carboranes.[381]

Chemical Properties

GENERAL

The unusually reactive nature of diborane(6) and the numerous and varied types of reactions in which it participates confer upon it exceptional chemical complexity and interest. A compilation of information covering the data available in early 1963 is to be found in a published chapter on the boron hydrides[212], and two earlier accounts of certain aspects of the chemistry of B_2H_6 are worthy of mention.[382–3] Subsequent advances have been particularly numerous and demand a reappraisal of the state of knowledge.

Two circumstances govern the chemistry of diborane(6) to a profound degree. The first is that the molecule is electron deficient, which has very important chemical consequences, including the fact that the compound is associated with a wide variety of reactions that have unusually low activation energies. This state of affairs in turn confers upon diborane(6) a truly rare kind of chemical versatility that enables it to react readily with the majority of known substances: indeed, it must be numbered among the most reactive compounds known, and is certainly one of the most chemically versatile. Reactions in which it participates rarely require external heating and often occur well below room temperature, that is to say, at temperatures very much lower than those usually required by methane, for example. Yet the reactions of B_2H_6 are for the most part not violent and can be readily controlled, which is doubtless ascribable to the fact that it is a gas at ordinary temperatures and thus is a reactant that is not normally present in high concentration. A beneficial result of the lower temperatures required is that competing reactions become less likely and both product purity and yields are accordingly higher.

The other circumstance that has a profound influence on the chemistry of diborane, and which indeed dominates the chemistry of boron in general, is the exceptionally high affinity that this element displays for fluorine, oxygen and, to a lesser extent, nitrogen. The boron atoms will therefore often shed attached hydrogen atoms or organic groups if, for instance, they can be replaced by oxygen, more especially in the form of a hydroxy or alkoxy group. This is a factor which frequently governs the direction of a reaction in a predictable manner, and results in such changes as alkyl-transfer reactions, to mention one example.

Because of the complexity of the situation, the reactions of diborane are somewhat difficult to classify conveniently. Thus, except for a relatively few substitution reactions they can be divided into three main types, namely reactions in which the B_2H_6 molecule undergoes (*a*) symmetric cleavage to $2BH_3$ (which may be followed by further cleavage of the BH_3 to $—BH_2$ plus $—H$), (*b*) asymmetric cleavage to BH_2^+ (coordinated) plus BH_4^-, and (*c*) complete disruption. Such a broad classification is of comparatively little practical service, however, and for the purpose of this treatise it is more useful to consider firstly conversion to other boranes, secondly addition, thirdly substitution and finally other reactions, the last group being classified according to the second reactant. The order in which the second reactants appear in the text depends upon the identity of the atom at the believed bonding site and follows the order in the Periodic Table viewed by Groups.

CONVERSION TO OTHER BORANES

Of the available physical means listed on p. 78 for realizing the conversion of diborane(6) to higher boranes, thermal decomposition is by far the most convenient and the only method suitable for preparative purposes. Diborane(6) is an endothermic compound that requires only very moderate heating to cause it to decompose by reacting with itself bimolecularly (p. 135). The products of pyrolysis have been mentioned (p. 79), but since they are several in number, carefully controlled conditions are necessary to secure the optimum yield of any selected borane. It must be borne in mind that, apart from the solid polymer $(BH)_x$, thermally by far the most stable product is $B_{10}H_{14}$, with B_5H_9 next in order of stability. Both of these boranes are more stable than B_2H_6, while the remaining products are less stable: B_4H_{10} is even less stable than B_5H_{11}, both of which decompose relatively fast if stored at room temperature.

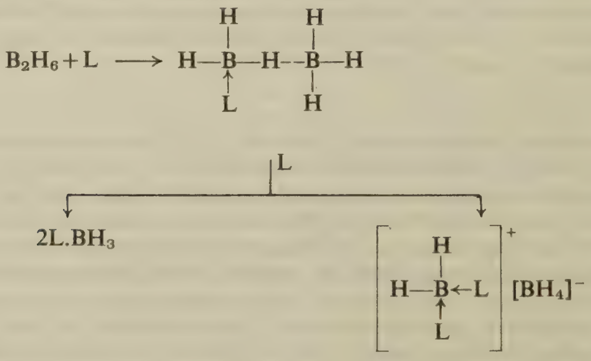
Tetraborane(10) is however the first isolable product, and a conversion of B_2H_6 to B_4H_{10} of up to 90% may be realized in a hot-cold reactor, in which an inner cylindrical surface is heated to 100°C, while the outer surface is maintained at -80°C to condense out the tetraborane as it is formed.[342] It had earlier been shown that pyrolysis at higher temperatures (180°C) leads to B_5H_{11} as a major product, whereas at still higher temperatures (250°–300°C) B_5H_9 predominates.[343] More recently a conversion to B_5H_9 of 57% was obtained in a single pass through a multistage flow reactor operating at 240°C with the diborane(6) admixed with five times its volume of hydrogen.[344] Some 14% of the diborane was lost as solid hydride, but 29% was recovered unchanged. It follows that, by recycling, an ultimate conversion to B_5H_9 of about 80% is realizable, as is indeed claimed for an alternative procedure at 205°C.[345] Under different conditions in a closed recycling system a conversion to $B_{10}H_{14}$ of 50–60% has been achieved[346], and a continuous process has been patented.[347] There is sound evidence for believing that $B_{10}H_{14}$ arises from the interaction of B_5H_9 with B_2H_6 and that B_5H_9 contributes half of the boron.[348–9] The solid hydride could arise from the further interaction of $B_{10}H_{14}$ with B_2H_6[350–1], but it could also partly originate from the decomposition of the intermediate *n*-B_9H_{15} via B_8H_{12} and B_6H_{10}.[17] The solid pyrolysis products may only in part be converted by aqueous KOH into KBH_4[384] and hence to B_2H_6 for recycling. The mechanistic aspect of the pyrolysis of B_2H_6 is discussed on p. 135, where it will be seen that the formation of higher boranes depends upon the prior formation of transient intermediates that defy isolation.

The effect of adding other substances to the pyrolyzing diborane(6) has received attention. For reasons mentioned on p. 80, solids are virtually useless, but gases may have a directional effect. Added hydrogen, although it retards pyrolysis, favours the production of B_5H_9[344], as mentioned above. Gases that behave as mild Lewis bases, however, such as dimethyl ether or carbon monoxide, definitely favour the production of $B_{10}H_{14}$.[385]

ADDITION REACTIONS

With Uncharged Species

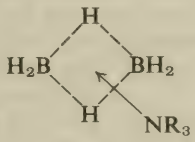
On account of its electron-deficient nature, diborane(6) possesses strong acceptor properties and reacts with Lewis bases generally, including some rather weak donors such as carbon monoxide. It is a stronger acceptor than pentaborane(9).[386] But in such acceptor reactions, the B_2H_6 molecule is ordinarily cleaved, especially in the presence of excess of the base. The diborane unit may be preserved, however, if (*a*) the donor atom of the base L is a first-row typical element such as nitrogen and thus possesses no *d* electrons, and (*b*) only 1 molecule of base per molecule of B_2H_6 is present, in which case it is sometimes possible to isolate an adduct of formula type $B_2H_6.L$. In the presence of excess base, however, the diborane(6) is normally cleaved by a second molecule of the base. Such cleavages may be symmetric and homolytic or, less commonly, asymmetric and heterolytic, according to whether the second molecule of the base attacks the second or first boron atom, respectively:



symmetric cleavage
(homolytic)

asymmetric cleavage
(heterolytic)

In the first stage the base attacks one of the boron atoms of the diborane(6) molecule nucleophilically. The first product, the singly bridged adduct $B_2H_6.L$, is, however, not always isolable, even under the most carefully controlled conditions, although in many cases there are good reasons for expecting it to occur as an unstable intermediate. Thus the original claim[387] concerning the existence of the intermediates $B_2H_6.NC_5H_5$ and $B_2H_6.NEt_3$ soon found support from chemical evidence for a corresponding intermediate with ammonia, $B_2H_6.NH_3$[388], and confirmation for the existence of the latter, as well as of $B_2H_6.NH_2Me$ and $B_2H_6.NMe_3$, was obtained by tensiometric titration.[389] Diborane(6) is thus a Lewis acid *per se*. Even with bases so weak that the reaction shows only slight tendency to proceed further, such adducts may have transitory existence; as an example, the species $B_2H_6.OEt_2$ has been proposed[138] to account for the very rapid proton exchange of B_2H_6 when dissolved in ether. The chemical and thermodynamic evidence for the existence of molecules of the type $B_2H_6.NR_3$ and the lack of boron isotope exchange between B_2H_6 and the borane(3) adduct $H_3B.NMe_3$ are in strong support of the singly bridged structure given above[389-90], rather than the alternative doubly bridged structure



once suggested.[391]

Adducts of type $B_2H_6.L$ [L = Lewis base] may also be formed by the action of diborane(6) on a borane(3) adduct $BH_3.L$

$$2BH_3.L + B_2H_6 \rightarrow 2B_2H_6.L$$

It has been demonstrated by isotope studies that for the instance of the trimethylamine adduct $Me_3N.BH_3$ this reaction takes place without the rupture of the B—N bond.[390]

The unstable adduct $B_2H_6.B_2Cl_4$ appears to be the first product of the reaction of diborane(6) with diboron tetrachloride B_2Cl_4 in ether at reduced temperatures, since the reaction stops when 1 mole of B_2H_6 has been taken up[318]

$$B_2H_6 + B_2Cl_4 \xrightarrow[Et_2O]{-23°C} B_2H_6.B_2Cl_4$$

Warming to room temperature, or removal of the ether, however, causes decomposition to a variety of products (p. 134).

(i) *Symmetric cleavage.*—Examples of symmetric cleavage are very common. The end effect of such reactions is that the B_2H_6 molecule has reacted as 2 molecules of borane(3) BH_3, which species, with its vacant orbital, is unquestionably to be regarded as a Lewis acid. The cleavage of the diborane(6) is normally symmetric when either (*a*) the base is sufficiently bulky to hinder the attack of a second molecule on the same boron atom, or (*b*) is more electropositive than hydrogen. With a strong base, a relatively stable solid complex with a comparatively low dissociation pressure is likely to result. Thus the adduct formed by trimethylamine has the formula $H_3B.NMe_3$[267] and exerts a vapour pressure of less than 1 Torr at 25°C. Many other products of this type are known that incorporate a variety of donor atoms from groups V and VI, such as $H_3B.NC_5H_5$[392], $H_3B.PPh_3$[393], $H_3B.AsMe_3$[394] and $H_3B.SMe_2$.[395] But the adduct formed with the much weaker Lewis base dimethyl ether, i.e. $H_3B.OMe_2$, has an appreciable dissociation pressure even at low temperatures (18 Torr at $-78{\cdot}5$°C), while in the vapour phase it is completely dissociated.[396] Further examples of borane(3) adducts are cited in the section on monoboranes on p. 11.

A mechanistically different case may be the reaction with carbon monoxide, which under pressure and at 90°–100°C cleaves diborane symmetrically to give borane(3) carbonyl $H_3B.CO$[267] in a reversible reaction. This compound is discussed in more detail on p. 15. In this case there is a total absence of evidence to indicate the formation of an initial intermediate of formula $B_2H_6.CO$, and the unusually high temperature required for reaction suggests that the mechanism is here dependent on the preliminary thermal dissociation of the B_2H_6:

$$2B_2H_6 \rightleftharpoons BH_3 + B_3H_9$$

$$BH_3 + CO \rightarrow H_3B.CO$$

There is also a total lack of evidence for intermediate adducts of type $B_2H_6.L$ when the donor element of the base L possesses *d* electrons. The original formulation of the phosphine adduct $B_2H_6.2PH_3$[397] was later shown to be incorrect.[398] It is in fact the monoborane adduct $H_3B.PH_3$ (p. 28), and all other known adducts obtained from substituted phosphines and arsines (p. 29), as well as from compounds of sulphur and selenium (p. 37), are of this type. The different behaviour has nothing to do with base strength as such, since towards boranes phosphines are stronger bases than amines, while organic sulphides and selenides are weaker. Neither, apparently, is the mechanism the same as that proposed above for the interaction of B_2H_6 with CO, since addition with the heavier donor elements ordinarily occurs without heating and often at low temperatures. Rather it appears as if no form of hydrogen bridge bonding that involves a boron atom linked by means of a dative bond to an element containing *d* electrons is sufficiently stable to survive, even temporarily.

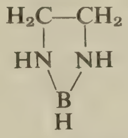
Symmetrical cleavage of B_2H_6 may also occur with bidentate and polydentate donors. Substituted diphosphines typified by P_2Me_4 and $P_2(NMe_2)_4$ give the bis-borane(3) adducts $P_2Me_4.2BH_3$[399–400] (p. 32) and $P_2(NMe_2)_4.2BH_3$[401], in which each boron atom is linked to a different phosphorus atom. The same is true of the adducts formed by the phosphorus methylimide $P_4(NMe)_6$, which have the formulae $P_4(NMe)_6.nBH_3$ [$n = 1$–4].[402] Though some bidentate nitrogen donors cleave B_2H_6 asymmetrically, hydrazine N_2H_4 cleaves it symmetrically[403–5] (p. 114) as do methylhydrazines.[403, 399, 406] Bisdimethylamino-methane and -silane similarly give the bis-borane(3) adducts $CH_2(NMe_2)_2.2BH_3$ and $SiH_2(NMe_2)_2.2BH_3$ respectively.[407]

A further group of compounds which effects symmetric cleavage of B_2H_6 is provided by the ylides of phosphorus, but not nitrogen. An example is $Ph_3\overset{+}{P}—\bar{C}H_2$[408–9] (p. 120). The boron links itself to the carbon. Ylides containing arsenic in place of phosphorus also react in a comparable way[410] (p. 120), as do initially those containing sulphur[411], though in the last case subsequent rearrangement occurs (p. 131).

(ii) *Asymmetric cleavage.*—Examples of asymmetric cleavage of diborane(6) are provided by the reactions with a number of nitrogenous bases, including ammonia, although it was a long time before the true position was understood. The solid of low volatility obtained originally in 1923 with ammonia[319] was demonstrated by molecular-weight determination in liquid ammonia not to be the monomeric species $H_3B.NH_3$, but to be dimeric.[412] After successive but unsuccessful attempts by various workers to explain the structure as ammonium salts of formulae $(NH_4)_2[B_2H_4]$[413] and $NH_4[H_2N(BH_3)_2]$[396], it was first reported[414] and then in a series of papers[388, 415–18] amply demonstrated that the compound is in fact a tetrahydroborate(1−) salt of formula $[H_2B(NH_3)_2][BH_4]$. A second compound of formula $[HB(NH_3)_3][BH_4]_2$ can also be formed.[418] Nevertheless the monomeric compound ammonia borane $H_3N.BH_3$ (p. 112) has been successfully prepared from tetrahydrofuran borane $C_4H_8O.BH_3$[419], from dimethyl sulphide borane(3) $Me_2S.BH_3$[420], and in other ways.[414, 416, 421] Ammonia borane (p. 18) is more volatile and can be sublimed in a vacuum.[416] In solution it is monomeric.[414] Methylamine also forms both kinds of adducts (p. 20), in that with diborane(6) it gives an imperfectly characterized non-volatile product (m.p. 5°–10°C)[422] showing an n.m.r. spectrum[423] and X-ray diffraction pattern[424] consistent with the formulation $[H_2B(NH_2Me)_2][BH_4]$[423], whereas with sodium tetrahydroborate it gives a volatile solid (m.p. 56°C), identified as $H_3B.NH_2Me_{425}$ (p. 20). In any case $[H_2B(NH_3Me)_2][BH_4]$ slowly rearranges to the monomer $H_3B.NH_2Me$[244], and this may indicate that even in many instances where symmetric cleavage appears to be the mode of reaction the initial cleavage by the base L is in fact asymmetric, the product actually isolated depending on the relative stability of the species $[H_2BL_2][BH_4]$ which is first formed. It would however be rash to assume that this is invariably the reaction path.

Dimethylamine also shares the power to cleave diborane asymmetrically[423], as well as symmetrically to give the simple adduct $H_3B.NHMe_2$ (pp. 20, 113), which is usually observed. Trimethylamine apparently lacks the capacity to cleave diborane asymmetrically, and gives only the monomeric adduct by symmetric cleavage. It does not follow that the cation $[H_2B(NMe_3)_2]^+$ is incapable of existence, for it can be prepared in other ways[426–7], as can cations of the types $[H_2B(PR_3)_2]^+$, $[H_2B(AsR_3)_2]^+$ and $[H_2B(SR_2)_2]^+$.[427] With B_2H_6 in tetrahydrofuran, lithium hydrogen sulphide LiHS reacts directly to form two compounds which give rise to the ions $[H_2B(SH)_2]^-$ and $[H_3BSH]^-$ respectively, showing that in this instance diborane exhibits both asymmetric and symmetric cleavage.[428] Asymmetric cleavage is also effected by dimethyl sulphoxide to give $[H_2B(OSMe_2)_2]^+[BH_4]^-$.[429] In the presence of iodine, ether will cleave diborane asymmetrically to give the cation $[H_2B(OEt_2)_2]^+$.[430] Even on their own some ethers R_2O can apparently cause a slight measure of asymmetric cleavage, presumably to the ions $[H_2B(OR_2)_2]^+$ and $[BH_4]^-$, since dissolved diborane causes the ethers to conduct an electric current.[431]

Bidentate donors may also effect asymmetric cleavage of diborane, but this is not finally established. Two adducts of ethylenediamine, of constitution $C_2H_4(NH_2)_2.BH_3$ and $C_2H_4(NH_2)_2.B_2H_6$, have been prepared by an indirect method.[432] From their infra-red spectra it was concluded that the former has the simple chain structure and the latter an ionic structure with a cyclic cation $[H_2B(NH_2CH_2)_2]^+[BH_4]^-$. This, however, has been disputed[433–4], since, irrespective of whether the latter compound is prepared by the indirect or direct method, its ^{11}B n.m.r. spectrum indicates the open-chain structure of the bis-borane adduct $H_3B.NH_2C_2H_4NH_2.BH_3$ in the *trans* configuration, corresponding to symmetric rather than asymmetric cleavage of the diborane. The evidence is clearly conflicting. It has moreover been claimed[435] that even the monoborane adduct is cyclic and at 20°C loses hydrogen vigorously to give the cyclic compound



The position requires further study, for the original monoborane adduct[432] was apparently much more stable. Also it has been found[435] impossible to repeat the indirect preparation of the original diborane(6) adduct $C_2H_4(NH_2)_2.B_2H_6$, even with excess diborane, whereas the earlier workers reported no difficulty in preparing it and noted that it requires to be heated to 89°C before it begins to decompose.[265]

With Charged Species

The electron deficiency of diborane(6) enhances its tendency to add to negatively charged ions. It was discovered by H. C. Brown and co-workers[387, 234] that solutions of alkali metal tetrahydroborates in diglyme absorb diborane(6). The explanation given is that the latter cleaves symmetrically in reacting additively with the BH_4^- anion:

$$2BH_4^- + B_2H_6 \rightarrow 2B_2H_7^-$$

It is possible to isolate sodium heptahydrodiborate(1−) NaB_2H_7 as a solvate from solutions in various polyethers, but attempts to remove the last molecule of solvent invariably lead to its complete decomposition.[238] This is quite generally true of the salts of smaller cations, but with bulkier cations unsolvated crystalline salts can be isolated, e.g. $[NBu_4]^+[B_2H_7]^-$[436] and $[NEt_4]^+[B_2H_7]^-$.[437] For further information concerning the heptahydrodiborate(1−) anion and its salts, see p. 141.

Diborane(6) reacts similarly with salts containing the AlH_4^- ion by simple addition of a BH_3 unit to produce salts of the $AlBH_7^-$ anion.[438] This ion is presumably similar in structure to $B_2H_7^-$, and is said to rearrange to the more stable $[AlH_3(BH_4)]^-$ ion. Other ionic double hydrides react similarly with diborane to give triple hydrides.[439] With the silyl anion SiH_3^- diborane(6) apparently gives the adduct ion $[SiH_3.BH_3]^-$, which is unstable and decomposes into BH_4^-, SiH_4 and condensed species.[440] Likewise, with the germyl anion GeH_3^- $[GeH_3.BH_3]^-$ is formed.[441] Addition of BH_3 also occurs with the ions $RCOO^-$[442], CNO^-, R_2NCS^-, $C(CN)_3^-$ and $N(CN)_2^-$.[443] The thiocyanate ion SCN^- reacts similarly[444], as apparently does the azide ion N_3^- in the first instance, especially in the form of its lithium salt LiN_3[445], although the product is unstable. The fluoride ion gives the fluorotrihydroborate ion $[BH_3F]^-$.[444] The cyanide ion is exceptional in adding on two BH_3 groups to give the ionic species $[BH_3CN.BH_3]^-$.[444] However, the mono-adduct $[BH_3CN]^-$, first isolated as a dioxanate of the lithium salt[446–7], is also obtainable, and this has been studied from the standpoint of hydrolysis[448–9], hydrogen exchange[448], reducing powers[449–51] and spectrum[449], as well as from the standpoint of the complexes it forms. Thus with the bis(ethylenediamino)nickel(II) cation $[Ni(en)_2]^{2+}$ the nitrogen atoms coordinate to the metal atom to form the complex $(C_2H_4(NH_2)_2)Ni(NCBH_3)_2$[452], while with nitrogen donors such as trimethylamine the boron acts as an acceptor to give ultimately the complex $Me_3N.BH_2CN$, a negatively charged hydride ion having been displaced in the course of the reaction.[453]

With the thiolotrihydroborate (l–) anion $HSBH_3^-$, diborane(6) apparently gives a new unstable ion of formula $HS(BH_3)_2^-$ [454]:

$$HSBH_3^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-78°C} HS(BH_3)_2^-$$

In its reactions with some ions, B_2H_6 provides further evidence of the relationship between the species BH_3 and the isoelectronic oxygen atom. Thus it reacts with the anion of sodium hyponitrite $Na_2N_2O_2$ to give the boranonitrite $Na^+[NO(BH_3)]^-$ [455], which is isoelectronic with $NaNO_2$.

That B_2H_6 can even react with certain metal carbonyl anions to give compounds in which BH_3 acts as a ligand, has been reported[456], and salts of the complex manganese and rhenium anions $[H_3BMn(CO)_5]^-$, $[H_3BMn(CO)_4(PPh_3)]^-$, $[H_3BRe(CO)_5]^-$ and $[(H_3B)_2Re(CO)_5]^-$ have been prepared. There is evidence that the cobalt anion $[Co(CO)_4]^-$ forms a similar borane complex at low temperatures, but this is very unstable and was not isolated. Compounds formed with the carbonyls of metals in group VII and of cobalt, rhodium and iridium have been the subjects of a patent.[457] For such transition-metal species to be stable, the metal atom probably needs to have a high complement of electrons, as in these instances cited. In the rhenium ion $[(H_3B)_2Re(CO)_5]^-$ the second BH_3 group is not necessarily linked to the rhenium atom to give a 7-coordinated structure. It could be linked to the first BH_3 group via a single hydrogen bridge, in which case this is the first example known in which undissociated B_2H_6 acts as a ligand and the ion should be written $[B_2H_6.Re(CO)_5]^-$. Alternatively it might be linked in some surprising and unpredictable way, as is the case with the manganese compound $(H_3B)_2Mn_3H(CO)_{10}$.[458] A structural determination of the $[(H_3B)_2Re(CO)_5]^-$ ion is therefore an interesting prospect.

SUBSTITUTION

By Organic Groups

The simplest form of substitution undergone by diborane(6) is the replacement of hydrogen by deuterium, and an account of this is given on p. 138. Replacement of hydrogen by alkyl and other organic groups can be realized in a variety of ways. With boranes that exchange BH_3 units, diborane(6) and its derivatives will also exchange alkyl groups reversibly at or near room temperature, presumably by the transference of BH_2R units: thus this occurs with alkyl derivatives of B_4H_{10}[459–60] and B_5H_{11}[461, 459] but not those of B_5H_9 or $B_{10}H_{14}$.[461] Only the terminal hydrogen atoms of B_2H_6 can be substituted by organic groups, so that compounds of formula $B_2H_{6-n}R_n$ $[n=1–4]$, but no penta- or hexa-substituted derivatives, are known. If attempts are made to prepare the latter, disproportionation with bridge rupture occurs and a trisubstituted borane(3) is one of the products. Otherwise than in aluminium compounds such as the trimethylaluminium dimer Al_2Me_6, bridging methyl groups are not found between boron atoms, although the possibility has been investigated theoretically.[462] Substitution of any or all of the terminal hydrogen atoms of B_2H_6 by organic radicals does not normally break the hydrogen bridge, so that monomeric $H_2BCH(CMe_3)CH_2CMe_3$[463] is an oddity and presumably arises through steric factors. Trisubstituted boranes readily exchange their ligands with diborane(6)[271, 464], usually within hours at room temperature

$$(6-n)B_2H_6+2nBR_3 \rightleftharpoons 6B_2H_{6-n}R_n \quad [n = 1, 2, 3, 4]$$

and the kinetics of the B_2H_6-BMe_3 reaction have received study.[465-6] Such equilibrium reactions provide a particularly convenient way of preparing small quantities of many organic derivatives, as was first observed for the methyl compounds.[271] It follows, however, that disproportionation reactions such as

$$2B_2H_3R_3 \rightleftharpoons B_2H_4R_2+B_2H_2R_4$$

will occur and lead to the establishment of redistribution equilibria involving all the possible species. For the methyldiboranes such equilibria are established at room temperature in a few hours in the gas phase[171], but the activation energies are such that the pure compounds can be isolated by fractionation at low temperatures and can be stored for prolonged periods at $-78{\cdot}5°C$. For the disubstituted derivatives both 1,1- and 1,2-isomers are known[467], with the latter capable of existing in *cis* and *trans* forms.[468] The 1,1-isomers are prepared from trialkylboranes and B_2H_6[271], whereas the 1,2-isomers can be prepared from the monoalkyldiboranes by disproportionation.[469] The 1,2-isomers are less volatile and kinetically much more stable than the 1,1-isomers, thus disproportionating much more slowly than the latter. Whether they are also thermodynamically more stable is not known. Equilibrium reactions involving various alkyldiboranes have been investigated[171, 465-6, 469-70], for example

$$3B_2H_2Me_4 \rightleftharpoons 2B_2H_3Me_3+2BMe_3$$

Several other methods for preparing alkyldiboranes are available. Instead of allowing trialkylboranes to react with B_2H_6, they can be made to react with molecular hydrogen, either by the application of elevated temperatures and high pressures[471-2] or by the use of a silent electric discharge[473], e.g.

$$2BR_3+5H_2 \xrightarrow{180°\text{–}200°C} B_2H_5R+5RH$$

Or, when caused to react with tetraborane(10) B_4H_{10}, trialkylboranes will also give diborane(6) derivatives such as $B_2H_2R_4$ along with a B_2H_4 polymer.[31] The interaction of olefins with B_2H_6 to produce alkylated diboranes is an application of hydroboration, which is discussed more fully on p. 103. Thus with ethylene the first product is B_2H_5Et[474-5]

$$B_2H_6+C_2H_4 \rightarrow B_2H_5C_2H_5$$

but the reaction proceeds further to give successively $B_2H_4Et_2$, $B_2H_3Et_3$, $B_2H_2Et_4$ and BEt_3. The same method has been used to prepare mixed alkylated boranes, e.g. BMe_2Et from $B_2H_2Me_4$ and C_2H_4[476], and in principle could also produce mixed diborane(6) derivatives:

$$B_2H_4Me_2+2C_2H_4 \rightarrow B_2H_2Me_2Et_2$$

The hydroboration reaction has also been used to produce derivatives containing bulkier alkyl groups.[477] With organometallic compounds the transference of organic ligands to boron sometimes takes place, as, for example, with tetramethyllead:

$$B_2H_6+PbMe_4 \rightarrow B_2H_5Me+PbHMe_3$$

This reaction occurs at room temperature in 1,2-dimethoxyethane and proceeds further.[478] Vinyl groups can similarly be transferred to boron from tetravinyllead $Pb(C_2H_3)_4$, but with B_2H_6 reduction simultaneously occurs with the formation of B_2H_5Et.[479] Tetraalkyldiboranes are one of the products of interaction of diborane(6) with alkoxydialkylboranes R_2BOR'.[480] Likewise 1,2-diphenyldiborane is produced from chlorodiphenylborane Ph_2BCl and B_2H_6 in hexane.[481] Other methods depend upon reduction. Thus alkyldiboranes are formed on the reduction of trialkylboroxines $(BRO)_3$ by dialkylaluminium hydrides $AlHR'_2$ [482], of BEt_2Cl by NaH[483], and of BCl_3 by Al and gaseous H_2 in the presence of methyl iodide as a methylating agent.[484]

Alternatively alkali metal tetrahydroborates may be used as starting material. Thus alkyldiboranes are produced from the reaction of trialkylboranes with $NaBH_4$ and BF_3 in tetrahydrofuran[485], but when preparing larger quantities it is more convenient to dispense with the solvent and to heat the tetrahydroborate with the appropriate trialkylborane plus anhydrous HCl in an autoclave[486-7, 171]:

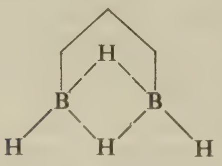
$$NaBH_4 + 3BR_3 + HCl \rightarrow 2B_2H_2R_4 + NaCl + RH$$

$$2LiBH_4 + 4BR_3 + 2HCl \rightarrow 3B_2H_2R_4 + 2LiCl + 2H_2$$

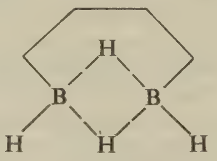
Anhydrous aluminium chloride improves the yield. Alternatively the trialkylborane may be replaced by a trialkylaluminium AlR_3.[488–9]

$$6LiBH_4 + 4AlR_3 + 18HCl \rightarrow 3B_2H_2R_4 + 6LiCl + 4AlCl_3 + 18H_2$$

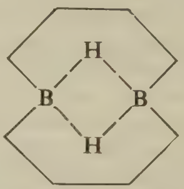
Alicyclic and aromatic derivatives of diborane have received little study, but preparations of the cyclohexyl[472], phenyl[490, 472], *p*-chlorophenyl[491] and naphthyl[491] compounds have been reported. An interesting development has been the preparation of cyclic organodiboranes, namely μ-polymethylenediboranes such as 1,2-trimethylene-, 1,2-tetramethylene- and bis(1,2-tetramethylene)-diborane(6)[492–8],



1,2-trimethylene-diborane(6)



1,2-tetramethylene-diborane(6)



bis(1,2-tetramethylene)-diborane(6)

which are prepared along with other compounds through the interaction of allene and 1,3-butadiene respectively with B_2H_6. Although the tetramethylene compounds were originally formulated with C_4B five-membered borolane rings, ^{11}B n.m.r. spectra have clearly established the structures given above in the case of the first two compounds.[492, 499] For the bis(1,2-tetramethylene) compound, the above structure was first proposed for chemical reasons[500], since the hydrogen-bridge bonding between the boron atoms is unusually stable, while the compound, unlike tetraalkyldiboranes, does not hydroborate terminal olefins, and is stable at room temperature towards hydrolysis, alcoholysis and atmospheric oxidation.[494–5] Confirmation of the structure was subsequently provided by the molecular weights of the bis adducts obtained with several amines, for they were consistently about twice as high as those of the adducts that would have been obtained with hydrogen-bridge rupture from bis-borolane.[501–2] The above trimethylenediborane shows signs of ring strain and polymerizes rapidly in the liquid phase.[492] Bis(1,2-polymethylene)diboranes containing chains of more than 4 carbon atoms can be prepared from the appropriate terminal dienes, but a ring containing 6 or more carbon atoms is changed by thermal action into a more stable one with only 5 carbon atoms.[494]

Attempts to prepare trifluoromethyl-substituted diboranes have been reported.[503] Some of the ways of converting diborane(6) into its organosubstituted derivatives are listed in Table XII.

Table XII.—The Conversion of Diborane(6) to its Organosubstituted Derivatives

Reactant	Products	Ref.
BR_3	$B_2H_{6-n}R_n$ [n=1–4](a)	271, 464
C_2H_4	$B_2H_{6-n}Et_n$ [n=1–4], BEt_3	31, 474, 475
$PbMe_4$	B_2H_5Me, etc.	478
$PbVi_4$	B_2H_5Et, etc.	479
R_2BOR'	$B_2H_2R_4$, etc.	480
Ph_2BCl	1,2-$B_2H_4Ph_2$, etc.	481
Allene C_3H_4	1,2-trimethylenediborane(6)	492
Terminal diolefin	1,2-polymethylene- and bis(1,2-polymethylene)-diborane(6)	493, 494, 499, 501
B_4H_9Me	B_2H_5Me, etc.(a)	459, 460
$B_5H_{10}R$, $B_5H_9R_2$	B_2H_5R, etc.(a)	461, 459

(a) Formed reversibly.

Table XIII.—Physical Properties of Some Alkyldiboranes

Compound	m.p. (°C)	b.p.[a] (°C)	vapour pressure (Torr)	log p(Torr) $= -A/T+C$		ΔH_{vap} (kcal mol^{-1})	Ref.
				A	C		
B_2H_5Me			55 (−78·5°C)				271
1,1-$B_2H_4Me_2$	−150·2	−2·6	10 (−78·5°C)	1,212	7·363	5·540	271
1,2-$B_2H_4Me_2$	−124·9	+4·9	81·6 (−43·2°C)	1,290	7·532	5·902	467
$B_2H_3Me_3$	−122·9	45·5	123 (0°C)	1,527	6·673	6·980	271
$B_2H_2Me_4$	−72·5	68·6	48 (0°C)	1,643	7·687	7·525	271
B_2H_5Et			7 (−78·5°C)				464
1,1-$B_2H_4Et_2$	—[b]	67·1	42 (0°C)	1,760	8·055	8·045	464
1,2-$B_2H_4Et_2$			36 (0°C)				469
$B_2H_3Et_3$			·4 (0°C)				464
$B_2H_2Et_4$	−56		0·5 (0°C)				464
B_2H_5(*n*-Pr)			6·2 (−60°C)				464
1,1-B_2H_5(*n*-Pr)$_2$			2·8 (0°C)				464

(a) Extrapolated.
(b) Sets to a glass at low temperatures.

Physical studies of organo derivatives of diborane(6) are still sparse. Physical properties of some of the simpler alkyldiboranes are given in Table XIII. The n.m.r. spectra of alkyldiboranes have been systematically investigated with regard to the influence of alkyl substitution.[504] Generally, proton resonances from α-CH_2 groups attached to boron are found upfield from the resonances associated with methylene protons in alkanes. Mass-spectral patterns have been published for several alkyldiboranes.[10, 505] Electron diffraction experiments with tetramethyldiborane(6) $B_2H_2Me_4$ have resulted in an accurate set of molecular parameters and demonstrated that the methyl groups are not freely rotating.[506] Infra-red spectra of methyl-[507–12] and ethyldiboranes[513, 508–10] have been measured and vibrational assignments made; assignments have also been made for the Raman frequencies of four of the methyl compounds.[514, 123–4]

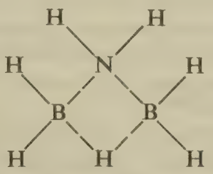
By Miscellaneous Groups or Atoms

Boron readily forms stable covalent bonds with elements in groups V, VI and VII, and on account of the possibility of π bonding these are frequently stronger than the corresponding bonds formed by carbon. The state of knowledge regarding reactions leading to the formation of B—N, B—P, B—As, B—Sb, B—O, B—S, B—Se and B—halogen bonds was reviewed in 1960[515], but has been extended considerably since.

The simplest nitrogen-substituted derivative of diborane(6) is aminodiborane(6) $H_2NB_2H_5$. It is a stable monomeric compound readily prepared by the action of diborane(6) on its diammine[516]

$$B_2H_6 + B_2H_6.2NH_3 \xrightarrow{85°C} 2B_2H_5NH_2 + 2H_2$$

It melts at −66·4°C, has an extrapolated b.p. of 76·2°C and a Trouton constant of 21·0 cal mol^{-1} K^{-1}. The apparent absence of association by hydrogen bonding, which would be expected with 3-coordinate nitrogen, might be regarded as indicative that the nitrogen atom has a different environment in this compound. According to early suggestions[517–18], the amino group occupies a bridge position



as has since been demonstrated for both μ-$H_2NB_2H_5$ and μ-$Me_2NB_2H_5$ by electron diffraction[519], and for μ-$Et_2NB_2H_5$ by infra-red spectroscopy[520], even though the vibrational spectra of μ-$Me_2NB_2H_5$ are inconclusive.[521] The NH_2 group is not in the plane of the BNBH ring: rather, the appearance of only one type of boron atom in the ^{11}B n.m.r. spectrum of the monomethylamino compound μ-$HMeNB_2H_5$[522] suggests that it is perpendicular to the plane of the ring and symmetrically oriented with respect to the two boron atoms. This also agrees with the orientation of the NC_2 group in μ-$Me_2NB_2H_5$, as determined by electron diffraction.[519] The dimethylamino compound was first prepared by heating bis(dimethylamino)diborane(6) with B_2H_6[518]

$$(Me_2N)_2B_2H_4+B_2H_6 \xrightarrow{80°C} 2Me_2NB_2H_5$$

but aluminium tetrahydroborate(1 −) $Al(BH_4)_3$ also effects the conversion.[523] Alternatively it may be prepared in one of several other ways, including the action of B_2H_6 on bis(dimethylamino) sulphide[524] or sodium dimethylamidotrihydroborate(1 −)[525]:

$$(Me_2N)_2S+B_2H_6 \rightarrow Me_2NSH+\mu\text{-}Me_2NB_2H_5$$

$$Na[BH_3NMe_2]+B_2H_6 \rightarrow NaBH_4+\mu\text{-}Me_2NB_2H_5$$

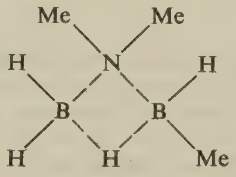
Additionally, use can be made of the fact that it is also one of the products obtained from the reversible disproportionation of dimethylaminoborane(3)[523]

$$3Me_2NBH_2 \rightleftharpoons (Me_2N)_2BH+\mu\text{-}Me_2NB_2H_5$$

It exchanges terminal hydrogen for methyl with trimethylborane(3) at 140°C to give μ-dimethylamino-B-methyldiborane(6)[526]

$$\mu\text{-}Me_2NB_2H_5+BMe_3 \rightleftharpoons \mu\text{-}Me_2NB_2H_4Me+\tfrac{1}{2}B_2H_2Me_4$$

This compound has m.p. −95°C and exerts a steady vapour pressure of 31·0 Torr at 0°C, whereas the vapour pressure of methyldiborane B_2H_5Me undergoes rapid change through disproportionation. The implication is, that the dimethylamino group forms a more stable bridging link than does the hydrogen atom. On the other hand, terminal substitution of the boron atoms by methyl groups definitely weakens the bridging system, as is clear from a comparison of the ^{11}B n.m.r. spectra of μ-$Me_2NB_2H_5$ and μ-$Me_2NB_2H_4Me$: that of the latter indicates the ring structure I only at low temperatures, whereas above −55°C the ring begins to rupture, and the compound consists mainly of the linear form II at and above −34°C.[526] By contrast μ-dimethylaminoborane(6) does not undergo such a reversible ring cleavage except at elevated temperatures and has a bridging system which is comparatively stable. The structure II for the methylated analogue confirms that the dimethylamino group is a stronger bridging group than the hydrogen atom in this compound.



I

$H_3B{\leftarrow}NMe_2{-}BHMe$

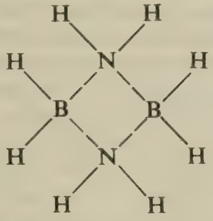
II

As is to be expected, μ-$Me_2NB_2H_5$ is a much weaker Lewis acid[527] than B_2H_6 on account of the bonding of the boron atoms with an atom possessing a lone pair of electrons, a circumstance that reduces the acceptor power of the boron. Nevertheless, adducts with pyridines, trimethylamine and substituted phosphines have been prepared.[527] N.m.r. studies demonstrate that μ-aminodiboranes undergo an intramolecular bridge and terminal hydrogen exchange that is accelerated by ethers.[522] The kinetics of the process have been elucidated.[528]

The simplest bis(amino)diborane(6) $(H_2N)_2B_2H_4$ is the dimer of boranamine (aminoborane(3)) BH_2NH_2, which for a long time was known only as a polymer (see p. 423). More recently it was discovered that a mixture of cyclic oligomers is obtained by adding sodium[529] or sodium amide[530] to the salt $[BH_2(NH_3)_2][BH_4]$ in liquid ammonia

$$NaNH_2+[BH_2(NH_3)_2][BH_4] \xrightarrow{\text{liq. NH}_3} \frac{1}{n}(BH_2NH_2)_n+NaBH_4+2NH_3$$

or by the interaction of $LiNH_2$ and B_2H_6 in ether.[531–2] The dimer is difficult to isolate, but the pentamer $(BH_2NH_2)_5$ is readily purified, and this on pyrolysis is partly converted to the cyclic dimer in poor yield.[530] The latter, however, is thermodynamically unstable with respect to the cyclic trimer, into which it is slowly transformed even at room temperature. Apart from the dimers, such oligomers are not structural derivatives of B_2H_6: nor, for that matter, are the linear polymers, which are also known (p. 423). No details have been reported about the physical properties of dimeric boranamine, which is $\mu\mu$-bis(amino)diborane(6)



except that it is a solid and sublimes *in vacuo* at 40°–45°C.

The substituted but largely dissociated derivative $\mu\mu$-bis(amino)tetramethyldiborane(6) $(H_2N)_2B_2Me_4$ has been obtained as a liquid by heating the adduct of ammonia and trimethylborane(3) in a sealed tube[533] and by the action of ammonia on diethylaminodimethylborane(3)[534]:

$$2Me_3B.NH_3 \xrightarrow[c.\ 20\ \text{atm}]{280°\text{C}} \mu\mu\text{-}(H_2N)_2B_2Me_4+2CH_4$$

$$2BMe_2NEt_2+2NH_3 \xrightarrow{-78°\text{C}} \mu\mu\text{-}(H_2N)_2B_2Me_4+2NHEt_2$$

Also the similar methylamino analogue $\mu\mu$-$(HMeN)_2B_2Me_4$ has been prepared by heating the first product of the interaction of excess methylamine with bromodimethylborane(3)[534]

$$2MeNH_2+BMe_2Br \xrightarrow{-78°\text{C}} [Me_2B(NH_2Me)_2]Br$$

$$2[Me_2B(NH_2Me)_2]Br \xrightarrow{>150°\text{C}} \mu\mu\text{-}(HMeN)_2B_2Me_4+2NH_3MeBr$$

These two diborane(6) derivatives have low bridge-bond dissociation energies of *c.* 10 kcal mol^{-1}.[533–4] As substitution at the nitrogen atom progresses through the series —NH_2, —NHMe, —NMe_2, the basic properties of the $\mu\mu$-bis(amino)diboranes decrease in accordance with expectation.

Bis(dialkylamino)diboranes are also volatile compounds, in which both dialkylamino groups occupy bridge positions.[517] Although this is not clear from a study of the crystal structure of the unsubstituted bis(dimethylamino) compound $(Me_2N)_2B_2H_4$[535], a 4-membered ring structure has been established for the chlorinated analogue $(Me_2N)_2B_2Cl_4$.[536–8] Several methods are now available for preparing $\mu\mu$-bis(dialkylamino)diboranes, including the action of diborane(6) on dialkylamines[517], bis(dialkylamino)boranes[523] or tetrakis(dimethylamino)diborane(4)[539], and the pyrolysis of tetramethylhydrazine bis-borane(3)[399]:

$$B_2H_6+2NHR_2 \xrightarrow{190°\text{C}} \mu\mu\text{-}(R_2N)_2B_2H_4+2H_2$$

$$B_2H_6+2BH(NR_2)_2 \xrightarrow{100°\text{C}} 2\mu\mu\text{-}(R_2N)_2B_2H_4$$

$$2B_2H_6+2B_2(NMe_2)_2 \xrightarrow{-23°\text{C}} \mu\mu\text{-}(Me_2N)_2B_2H_4+\text{products}$$

$$R_4N_2.2BH_3 \xrightarrow{100°\text{C}} \mu\mu\text{-}(R_2N)_2B_2H_4+H_2$$

The $\mu\mu$-bis(dialkylamino)diboranes are in equilibrium, at least in the liquid and vapour phases, with the monoborane(3) species (pp. 113, 425), e.g.:

$$(\mathrm{Me_2N})_2\mathrm{B_2H_4} \rightleftharpoons 2\mathrm{Me_2NBH_2}$$

The enthalpy of dissociation of the bis(dialkylamino) derivative, *c*. 20 kcal mol^{-1}[517], has been calculated from dissociation-pressure data, but this has since been corrected to allow for the accompanying disproportionation reaction, and a new free-energy equation for the dissociation has been derived[523], viz.

$$\Delta G^\circ_T = 20{\cdot}74 - 0{\cdot}0509T \text{ kcal mol}^{-1}$$

The enthalpies of dissociation in the liquid phase have been determined for a number of analogues by means of n.m.r. techniques.[534] The values are generally lower than for $(\mathrm{Me_2N})_2\mathrm{B_2H_4}$ and are spread over a wide range, as shown in Table XIV. It appears that the inductive effects, though important, are to some extent masked by steric factors, which often play a more important role. Such $\mu\mu$-bis(amino) derivatives of diborane(6) are thus dimers of the corresponding substituted boranamine (pp. 425, 431). The disproportionation reactions of bis(dimethylamino)diborane[523] and also its conversion by means of Lewis bases to the compounds $(\mathrm{Me_2N})_2\mathrm{BH}$ and $(\mathrm{Me_2N})_3\mathrm{B}$[527], neither of which form amino bridges, have been studied.

Table XIV.—Bridge-bond Energies and Entropies of Dissociation of Certain $\mu\mu$-Bis(amino) Derivatives of Diborane(6)

Compound	Temperature (°C)	$D^{(a)}$ (kcal mol^{-1})	$\Delta S^{(a)}$ (cal mol^{-1} K^{-1})
$\mu\mu$-$(\mathrm{H_2N})_2\mathrm{B_2Me_4}$	20	10·7$^{(b)}$	39·2$^{(c)}$
$\mu\mu$-$(\mathrm{H_2N})_2\mathrm{B_2Et_4}$	20	9·4	33·2
$\mu\mu$-$(\mathrm{HMeN})_2\mathrm{B_2Me_4}$	−10	10·7	40·8
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2H_4}$	90	20·74$^{(d)}$	50·9$^{(d)}$
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2H_2Me_2}$	20	11·0	30·0
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2Me_2F_2}$	0	8·8	34·0
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2Me_2Cl_2}$	50	11·9	43·1
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2Me_2Br_2}$	60	18·3	60·2
$\mu\mu$-$(\mathrm{Me_2N})_2\mathrm{B_2Cl_4}$	110	10·8	33·9
$\mu\mu$-$(\mathrm{Et_2N})_2\mathrm{B_2H_4}$	160	13·2	27·0
$\mu\mu$-$(\mathrm{Et_2N})_2\mathrm{B_2F_4}$	65	18·9	48·3
$\mu\mu$-$(n\text{-}\mathrm{Bu_2N})_2\mathrm{B_2H_4}$	120	15·4	37·8
$\mu\mu$-$(n\text{-}\mathrm{Bu_2N})_2\mathrm{B_2F_4}$	50	15·9	46·1

(a) As determined from n.m.r. measurements on the liquid phase in Ref. 534.

(b) The value for the vapour phase is 10·2 kcal mol^{-1} as obtained from pressure measurements at a mean temperature of −6°C in Ref. 533.

(c) The value for the vapour phase is 53·9 cal mol^{-1} K^{-1} as calculated from the relationship between the equilibrium constant and temperature over a range centred at −6°C in Ref. 533.

(d) As determined from pressure measurements on the vapour phase after correction for a competing equilibrium in Ref. 523.

As was seen on p. 92 for a mono-μ-aminodiborane(6), the nitrogen bridges in $\mu\mu$-bis(amino)diboranes are less likely to survive when the terminal hydrogen atoms on the boron atoms are progressively substituted by alkyl groups: thus B-substituted boranamines of type $\mathrm{R_2BNH_2}$ (p. 432) are essentially monomeric in the vapour phase, but in the liquid phase slowly establish a monomer-dimer equilibrium, which even at reduced temperatures lies markedly in favour of the monomeric form.[533]

It is not possible to replace more than two hydrogen atoms of $\mathrm{B_2H_6}$ by amino or substituted amino groups, since the bridge is so much weakened by further substitution that the molecule splits up into substituted monoboranes. This is also generally true when other atoms from groups V or VI are additionally substituted on to the boron: thus B-substituted diborylamines of type $(\mathrm{R_2B})_2\mathrm{NH}$ (p. 435) show no tendency to dimerize by forming amino bridges between boron atoms, though a measure of association by means of hydrogen bonding makes its appearance.[540] Substitution of one or more of the terminal hydrogen atoms of bis(dialkylamino)diboranes by a group-VII atom, however, probably on account of the relatively small steric requirements of the latter, never has such a marked effect and may even strengthen the bridge: thus the above-mentioned tetrachloroderivative $(Me_2N)_2B_2Cl_4$ still has a bridge-bond dissociation energy of 10·8 kcal mol^{-1}, as measured by n.m.r. equilibrium studies on the liquid phase[534], while the bridge bond in $(Me_2N)_2B_2F_4$ is even stronger, in fact too strong to measure by the same technique, and $(Me_2N)_2B_2Me_2F_2$, $(Me_2N)_2B_2Me_2Cl_2$ and $(Me_2N)_2B_2Me_2Br_2$ also have an appreciable bridge-bond stability.

Cyclic secondary amines of type $(CH_2)_nNH$ [$n=3$–5] can also be made to give μ-amino- and $\mu\mu$-bisamino-diboranes.[541] Attempts to prepare the aziridino derivatives [$n=2$] failed[541], although a trimeric form of aziridinoborane(3) has been characterized as the substituted cyclotriborazane $(BH_2N(CH_2)_2)_3$.[542]

Methylsilylamino- and disilylamino-diborane(6) have been prepared and studied.[543] Disilylaminoborane(3) is also known, both as a monomer and a dimer[543], but neither is well characterized. The physical properties of some of the μ-amino- and $\mu\mu$-bis(amino)-diboranes are presented in Table XV.

Azidoboranes (p. 116) are also preparable, and are formed, for example, by the interaction of sodium azide NaN_3 and B_2H_6 in diethyl ether.[445] They have been the subject of a detailed review.[545] The simplest azidoborane H_2BN_3 is not monomeric, the degree of association depending on the concentration. Cryoscopic measurements in benzene extrapolated to infinite dilution yield a molecular weight lying between that of the dimer and trimer[445], which suggests that a disubstituted diborane(6) may be one of the species present. The existence of such does not necessarily follow, however, and remains unconfirmed.

Phosphino derivatives of diborane(6) do not resemble the amino derivatives and have not been isolated as monomers. The unstable polymeric μ-phosphinodiboranes $(H_2PB_2H_5)_n$, $(HMePB_2H_5)_n$ and $(Me_2PB_2H_5)_n$ are involatile and known only in diethyl ether solution.[1005] Of these, only the last is stable in solution at room temperature, the others commencing to decompose a little above -10 and 0°C, respectively. In no case can the solvent be removed, even at reduced temperatures, without complete decomposition. Arsinodiboranes are unknown. It is doubtless relevant that phosphino and arsino monosubstituted derivatives of borane(3) are also not known as monomers or dimers, though stable cyclic trimers and tetramers as well as chain-like polymers are isolable[546] (pp. 118, 180 (Fig. 9), 181, 226).

The only known substituted derivatives of diborane(6) in which a group-VI atom is linked to boron are sulphur and selenium derivatives. Oxygen derivatives with either terminal hydroxyl groups or hydroxo bridges are unknown, probably because of their thermodynamic and especially their extreme kinetic instability with regard to disproportionation to diborane(6) and boric acid. All attempts to isolate hydroxyboranes have indicated that they also are not isolable. Nor are uncoordinated monoalkoxyboranes of formula BH_2OR known, either as monomers or dimers. Attempts to prepare these leads only to the disproportionation products B_2H_6 and either the dialkoxy- or trialkoxy-boranes $BH(OR)_2$ or $B(OR)_3$. These compounds are highly volatile and monomeric; e.g. the methyl compound $BH(OMe)_2$ has b.p. 25·9°C and Trouton constant 20·5 cal mol^{-1} K^{-1}.[272]

On the other hand, if the hydrogen atoms attached to the boron are substituted by alkyl groups, disproportionation is hindered to the extent that both series, the dialkylborinic acids BR_2OH and the alkylboronic acids $BR(OH)_2$, are easily isolable and show kinetic stability with respect to disproportionation. In the case of the borinic acids and their esters, the formation of hydroxo and alkoxo bridge between boron atoms might from *a priori* considerations be feasible, since there is a possibility that sufficiently strong residual acceptor properties could still remain with the boron atom. The infra-red spectrum of dimethylborinic acid BMe_2OH in the vapour phase[547–9] indicates that the vapour is monomeric. This is, however not true of the liquid, which has a b.p. of 56°C and a high Trouton constant of 29·7 cal mol^{-1} K^{-1}.[548] Vibrational spectra of the liquid[550] show a large reduction of *c.* 300 cm^{-1} for the O—H vibration, but also other changes that indicate this to be better explained by hydrogen bonding with oxygen

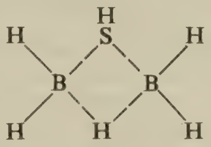
Table XV.—Physical Properties of Some μ-Aminodiboranes and μμ-Bis(amino)diboranes

Compound	m.p. (°C)	b.p.(a) (°C)	Vapour pressure (Torr)	$\log p(\text{Torr}) = -A/T + C$		ΔH_{vap} (kcal mol^{-1})	Trouton constant (cal mol^{-1} K^{-1})	Ref.
				A	*C*			
μ-$H_2NB_2H_5$	−66·4	76·2	32·3 (0°C)			7·300(b)	21·0	516
μ-$HMeNB_2H_5$		66·8	47·6 (0°C)			6·666(b)	19·6	518
μ-$Me_2NB_2H_5$	−54·4	50·3	101·4 (0°C)			6·670(b)	20·6	518
μ-$Me_2NB_2H_4Me$	−94·5		31 (0°C)					526
μ-$HEtNB_2H_5$	−96·4	86·6	19·31 (0°C)			7·686(b)	21·0	541
μ-$Et_2NB_2H_5$	−64	105·8	19 (24°C)					521, 520
μ-H(*n*-Pr)NB_2H_5	—(c)	121(d)	6·14 (0°C)	2,117	8·537	9·687	25·9	541
μ-$(CH_2)_3NB_2H_5$	−45·4	101	11·01 (0°C)			7·641(b)	20·2	541
μ-$(CH_2)_4NB_2H_5$	−63·5	121·8	14·03 (18·4°C)			8·223(b)	20·6	541
μ-$(CH_2)_5NB_2H_5$		148	26·92 (49·2°C)			8·352(b)	19·6	541
μ-$Me(SiH_3)NB_2H_5$	−39·0	51	5·38 (−43·4°C)	1,686	8·081	7·716	23·8	543
μ-$(SiH_3)_2NB_2H_5$	−68·8	54	74·5 (0°C)	1,669	7·974	7·640	23·3	543
μμ-$(Me_2N)_2B_2H_4$	73·5		33 (40·5°C)	2,721·4(e)	10·1970(e)	12·4(f)		517
μμ-$(Et_2N)_2B_2H_4$	43	120·2						544
μμ-(*n*-$Bu_2N)_2B_2H_4$	30		14 (72°C)					544
μμ-$((CH_2)_3N)_2B_2H_4$	51·8	186(d)	20·6 (70·5°C)	2,469	8·503	11·30	25·7	541
μμ-$((CH_2)_4N)_2B_2H_4$	34·2	194	14·46 (86·9°C)	2,705	8·675	12·38	26·5	541
μμ-$((CH_2)_5N)_2B_2H_4$	110	202	19·4 (114·9°C)	3,368	9·967	15·41	32·4	541
μμ-$((SiH_3)_2N)_2B_2H_4$			10 (25°C)					543

(a) Extrapolated unless otherwise indicated.
(b) Calculated from a vapour-pressure equation of form: $\log p(\text{Torr}) = -A/T + 1{\cdot}75 \log T - BT + C$.
(c) Sets to a glass below −143°C.
(d) Adjusted (as given in Ref. 541).
(e) For the solid.
(f) ΔH_{subl}.

rather than by oxygen bridging between two boron atoms, which would demand a change in the coordination number of the boron to 4 and in turn be associated with spectral changes that are not observed. The n.m.r. spectra[551–2] are also in accord with this conclusion, as in the demonstration that the degree of association of BMe_2OH in an inert solvent is complex and considerably greater than 2.[553] Moreover, the methyl ester BMe_2OMe, for which only oxygen bridge bonding, but not hydrogen bonding, is possible, shows itself to be strictly monomeric, which is not only in accord with its n.m.r. spectrum[552, 554], but also with its b.p. of 21°C and Trouton constant of 23·2 $cal\ mol^{-1}\ K^{-1}$.[546] Since neither hydroxo or alkoxo bridges are formed in these instances, they certainly would not be expected in boronic acids and their esters, in which the boron atom is linked to two oxygen atoms possessing lone pairs, a situation that would reduce its acceptor powers still further. The heavy association of methylboronic acid $BMe(OH)_2$, which melts at 92°C and has a vapour pressure of only 2·5 Torr at 25°C[549], is thus again due to hydrogen bonding. Its methyl ester $BMe(OMe)_2$ is, however, monomeric and is a liquid of b.p. 53·5°C.[555] Such internal coordinative saturation of the boron atom as occurs in all such cases thus proceeds through π bonding from the oxygen atom to which it is already linked. Rather persuasive confirmation of this is found in the low-temperature n.m.r. spectra of the dimethylborinic acid derivatives Me_2BOMe and $(Me_2B)_2O$, which indicates that the energy barriers to free rotation about the B—O bonds in these molecules amounts to *c.* 8·5 $kcal\ mol^{-1}$.[556]

Diborane(6) derivatives with substituents linked by sulphur are, however, known and show a structural resemblance to those containing nitrogen substituents. Like the $—NH_2$ and $—NR_2$ groups, the —SH and —SR groups occupy a bridge position in monosubstituted diborane(6). Thus the structure



has been demonstrated for the rather unstable μ-mercaptodiborane(6).[557–8] It has a m.p. of −101°C and an extrapolated b.p. of 53°C.[395] It is not prepared from B_2H_6 directly, but can be prepared from the salt $[NR_4]^+[HS(BH_3)_2]^-$, obtained from a tetraalkylammonium hydrogen sulphide and diborane(6), by treating it with hydrogen chloride:

$$NR_4HS + B_2H_6 \rightarrow [NR_4][HS(BH_3)_2]$$

$$[NR_4][HS(BH_3)_2] + HCl \rightarrow \mu\text{-}HSB_2H_5 + NR_4Cl + H_2$$

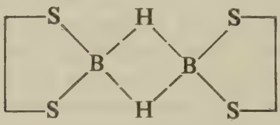
It is reactive and cleaves diethyl ether at room temperature.[557] Alkylthio bridges likewise occur, and the structure of (methylthio)diborane, prepared from the pyrolysis of polymeric methylthioborane(3) $(BH_2SMe)_x$, is similarly of the form μ-$MeSB_2H_5$.[559] It also is unstable and volatile, b.p. *c.* 60°C, and is monomeric.[395]

No derivatives of B_2H_6 are definitely known in which both bridge hydrogen atoms are replaced by mercapto or alkylthio groups. Thus alkylthioboranes are either trimeric, i.e. $(RSBH_2)_3$ in the condensed phase, and contain 6-membered $(BS)_3$ rings[559] (p. 130), or are a mixture of polymers that is insoluble in ether, benzene or chloroform.[392] However, in the vapour phase the methyl analogue $MeSBH_2$, at least, is approximately dimeric[395], but its structure is not known. The fully alkylated analogues are readily prepared, e.g. by exchange reactions in the presence of a catalyst[480]

$$(RS)_3B + 2BR'_3 \xrightarrow[130°\text{–}140°C]{B_2H_2(n\text{-}Bu)_4} 3RSBR'_2$$

The methylated derivative $MeSBMe_2$ is monomeric with m.p. −84°C and extrapolated b.p. 71°C.[395]

Bis(alkylthio)boranes $(RS)_2BH$ and trialkyl thioborates $(RS)_3B$ are also easily prepared[560], but do not dimerize with the formation of alkylthio bridges between boron atoms. Rather, compounds like $(EtS)_2BH$[561] and $(n\text{-}PrS)_2BH$[562], originally assumed to be dimeric and designated as tetrakis(alkylthio)diboranes, but later supposed to be cyclic trimers of $EtSBH_2$ and $n\text{-}PrSBH_2$[563], were later shown[559] from their n.m.r. and infra-red spectra to have their original analytical constitution, but to be associated by means of $B \leftarrow S$ coordinate bonds and not by hydrogen bridges. Where dimers occur, they are therefore not structural derivatives of diborane(6). In confirmation, 1,3,2-dithiaborolane $(CH_2S)_2BH$, which is associated in the condensed state, has an infra-red spectrum showing quaternary boron but no sign of $B{-}H_b$ frequencies[564], from which it follows that the structure is II, for example, rather than I; however, the physical properties suggest the additional presence of more highly associated forms in the condensed state.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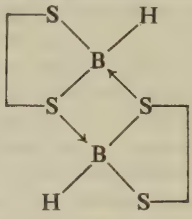

II

Although trialkyl selenoborates $B(SeR)_3$[565] and telluroborates $B(TeR)_3$[566] are known, no selenium- or tellurium-substituted derivatives of diborane(6) have been reported other than the unstable μ-methylselenodiborane(6) $MeSeB_2H_5$, in which the bridge bonding is under greater steric strain than in the sulphur analogue.[1004] Nevertheless, in toluene solution it is stabilized at room temperature by excess diborane(6) through reversal of the decomposition reaction

$$\mu\text{-}MeSeB_2H_5 \rightleftharpoons \frac{1}{n}(MeSeBH_2)_n + \tfrac{1}{2}B_2H_6$$

Inasmuch as some selenium derivatives of borane(3) are dimeric or exist as monomer-dimer equilibrium mixtures, e.g. $(Br_2BSeMe)_2$ and $(Br_2BSeEt)_2$[567], by analogy with the above sulphur compounds the dimers almost certainly owe their existence to coordinate rather than bridge bonding, and are thus not true derivatives of B_2H_6.

With halogen substitution, it is not possible to substitute more than one hydrogen atom of B_2H_6 without rupturing the hydrogen bridge, and even the monofluoro derivative B_2H_5F is unknown. An attempt to detect it in infra-red adsorption of B_2H_6-BF_3 mixtures after treatment over a large range of pressure and at temperatures up to 110°C failed[568], and the only intermediate observed was difluoroborane(3) HBF_2. On the other hand, the monohalogenodiboranes B_2H_5Cl, B_2H_5Br and B_2H_5I have all been isolated, although they rather readily disproportionate to B_2H_6 and, ultimately, the corresponding boron trihalide. The chloro compound has a m.p. of -143°C and an extrapolated b.p. of -11°C, and at atmospheric pressure the gas-phase disproportionation equilibrium requires about 70 h to be established at 35°C.[569] It can be prepared by the action of excess hydrogen on BCl_3 vapour in an electric discharge[270], or by treating B_2H_6 with HCl[270] or BCl_3.[320, 568] As this last equilibration reaction has been shown to proceed without any change in the number of molecules[317], it is correctly written[570]

$$B_2H_6 + BCl_3 \rightleftharpoons B_2H_5Cl + BHCl_2$$

B_2H_5Br, m.p. -104°C, b.p. (extrapolated) 10°C[269], is similarly produced from BBr_3[270, 571], and B_2H_5I, m.p. -110°C, v.p. 80 Torr at 0°C[572], from BI_3.[573] Alternatively B_2H_6 may be reacted with the hydrogen halide[571–2], in the case of HBr preferably in the presence of aluminium bromide[319–20], but only B_2H_5Br can conveniently be prepared from B_2H_6 and the free halogen[269, 320]; chlorine reacts too violently and iodine only very slowly, even on heating.[573] In all cases, the halogenodiborane needs to be separated from the reaction mixture by low-temperature fractionation or vapour-phase chromatography. The bromo derivative B_2H_5Br has been identified as a product from the reaction of boron atoms with HBr.[574]

It is rather surprising that no structural determinations have been carried out on B_2H_5Cl. From analogy with μ-B_2H_5SH one might expect the chlorine atom to occupy a bridge position. The evidence is however against this. It has been claimed that the microwave spectrum of B_2H_5Br can be explained only by assuming that the bromine atom is in a terminal position.[575–6] The ^1H and ^{11}B n.m.r. spectra have also been reported and clearly show two types of terminal hydrogen atoms and two different boron environments.[577] Comparison of the infra-red spectra of B_2H_5Cl and B_2H_5Br with that of B_2H_5Me also indicates structural analogies.[578] The infra-red spectrum of B_2H_5I shows close similarities with those of the chloro and bromo compounds.[573] In their physical and chemical properties the chloro compound is the least stable thermally and the most reactive, being spontaneously inflammable in air. All are however very reactive, and even B_2H_5I, which shows no tendency to inflame in air, hydrolyzes more rapidly than B_2H_6.[573] No dihalogeno derivatives of diborane(6) are known.

Table XVI summarizes the reactions of diborane(6) that result in the direct formation of substituted derivatives.

Table XVI.—Products of Some Substitution Reactions of Diborane(6)(a)

Reactant	Product	Ref.
$B_2H_6.2NH_3$	μ-$H_2NB_2H_5$	516
$H_3B.NH_2Me$	μ-$HMeNB_2H_5$	518
$H_3B.NH_2Et$	μ-$HEtNB_2H_5$	541
$H_3B.NH_2(n\text{-}Pr)$	μ-$H(n\text{-}Pr)NB_2H_5$	541
$\mu\mu$-$(Me_2N)_2B_2H_4$	μ-$Me_2NB_2H_5$	518
$Na[H_3BNMe_2]$	μ-$Me_2NB_2H_5$	525
$Me_4N_2.2BH_3$	μ-$Me_2NB_2H_5$	399
$(Me_2N)_2S$	μ-$Me_2NB_2H_5$	524
$H_3B.NH(CH_2)_3$	μ-$(CH_2)_3NB_2H_5$	541
$\mu\mu$-$((CH_2)_4N)_2B_2H_4$	μ-$(CH_2)_4NB_2H_5$	541
$\mu\mu$-$((CH_2)_5N)_2B_2H_4$	μ-$(CH_2)_5NB_2H_5$	541
NHR_2	$\mu\mu$-$(R_2N)_2B_2H_4$	517
$BH(NR_2)_2$	$\mu\mu$-$(R_2N)_2B_2H_4$	523
$B_2(NMe_2)_4$	$\mu\mu$-$(Me_2N)_2B_2H_4$	539
HCl	B_2H_5Cl	270
BCl_3	B_2H_5Cl	317
Br_2	B_2H_5Br	269
$HBr\ (+Al_2Br_6)$	B_2H_5Br	319, 320
BBr_3	B_2H_5Br	568
HI	B_2H_5I	572
BI_3	B_2H_5I	573

(a) See also Table XII.

REDUCING POWERS

General

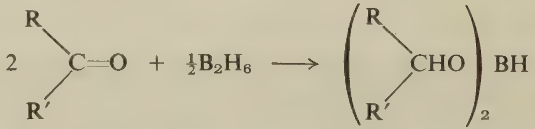
Diborane(6) is a very useful reducing agent with a wide application, and is on the whole a more powerful reagent than $NaBH_4$, but less so than $LiAlH_4$; however, in its mode of attack it differs from $NaBH_4$. This invests it with a certain selectivity. Thus, whereas $NaBH_4$ reacts principally by nucleophilic attack on an electron-deficient centre, B_2H_6, because it is already electron-deficient, preferentially attacks a molecule at a position of high electron density. Thus it will reduce azo compounds but, provided no coordinating agent is present, not chloral, probably because its C=O bond is adjacent to the strongly electron-withdrawing —CCl_3 group: with $NaBH_4$, however, the reverse is true. Again, B_2H_6 will reduce both —COOH and —COOR groups, whereas $LiBH_4$ reduces only the latter. In the study of compounds of biochemical origin this fact has been used as the basis of a diagnostic test for non-esterified carboxyl groups, but the test needs to be applied with care.[250]

An additional factor of great importance for reductions in general and especially for selective reductions is the catalytic effect of BF_3, even in traces, in enhancing the reducing powers of B_2H_6. This has on occasion even led to the formation of different products, depending on the method of generating the B_2H_6.[221–2] Many methods of preparation, e.g. Shapiro's method[280], use boron trifluoride etherate $F_3B.OEt_2$ as the starting material, and this inevitably means that the B_2H_6 is contaminated with traces of BF_3, which cannot readily be removed even by passing the gas through a solution of $NaBH_4$ in diglyme. If instead the B_2H_6 is prepared by the newer method which uses

$NaBH_4$ and I_2[264], no contamination by BF_3 is possible, and reproducible results are obtained in reduction experiments.[222] The effect of the BF_3 when present is possibly to promote reaction by forming a coordination complex with the reactant, which then has an enhanced reactivity towards diborane(6) or towards any borane(3) adduct that it forms with the solvent: alternatively a fluoroborane species such as BHF_2 or the etherate $R_2O.BH_2F$ may be involved. Because of this effect, the reducing properties of pure diborane(6) need a general reinvestigation, and this should be borne in mind when considering the rest of this digest of published work (see also pp. 101 and 127).

In reductions with diborane(6) the conversion is sometimes not completed in a single step, and the product may need working up with water or some hydroxyl-containing medium for the final stage. On account of its high reactivity, diborane(6) can effect reduction in several different ways. For example, the net effect may be simply to supply hydrogen, when the molecule that undergoes reduction commonly receives either two or four hydrogen atoms, with or without bond rupture; alternatively no hydrogen is transferred, but an atom of oxygen is removed; in other cases the net effect is both to supply two or four hydrogen atoms and remove one oxygen atom; or, less commonly, at least three atoms of hydrogen are supplied while a univalent atom or group is removed. It will suffice here to give some examples of each kind of reduction. Precise knowledge concerning the mechanisms is still largely lacking.

In reductions of the first class, the addition of hydrogen from the diborane(6) either reduces a multiple bond to a single bond, or effects the complete rupture of a bond, whether multiple or single. Ordinary aromatic rings are however not attacked. The addition of hydrogen across a double or triple bond never occurs in a single step, but as the result of subsequent protonolysis of the initial product, normally by means of a hydroxyl-containing medium. The diborane(6) reacts as borane(3) BH_3, which adds as —H and —BH_2 respectively to the two atoms participating in the multiple bond. Such an addition is known as *hydroboration*. This is of sufficient importance to treat separately (p. 103) for the case of homonuclear C=C and C≡C bonds, but the effect on heteronuclear multiple bonds is conveniently considered first. The boryl group BH_2 is most likely to add to the electron-richer atom, i.e. oxygen in the case of the C=O bond and nitrogen in the cases of the C≡N and C=N bonds. After protonolysis, the ultimate effect is to convert, e.g. the C=O group to CHOH, so that aldehydes[579] and ketones[579–82] become primary and secondary alcohols respectively. These changes occur via compounds of the type $(RCH_2O)_2BH$[583] in the former case and $(RR'CHO)_2BH$[583, 579] in the latter


$$2\,RR'C{=}O + \tfrac{1}{2}B_2H_6 \longrightarrow (RR'CHO)_2BH$$

The yields are usually good. The kinetics of the vapour-phase reaction with acetone have been studied[584], as have the stereochemistry and path of the reaction with 4-*t*-butylcyclohexanone.[585] Diborane(6) alone similarly converts the $>C{=}O$ group of lactones to the hydroxy compound, which is isolated as the hemiacetal, but in the presence of boron trifluoride etherate further reduction to $>CH_2$ occurs.[586] Other cases where reduction by diborane of $>C{=}O$ all the way to $>CH_2$ was achieved[587–8] were later recognized[222] to be due to the presence of BF_3. With *p*-benzoquinone the product of reduction with diborane is not a $>CHOH$ compound, but hydroquinone in almost quantitative yield.[589]

The C=N bond behaves like the C=O bond, so that oximes RR′C=NOH are reduced to N-alkylhydroxylamines RR′CH—NHOH[590–3], which may be reduced further to amines.[593] Likewise Schiff bases $RC_6H_4CH{=}NC_6H_4R'$ are reduced to secondary amines $RC_6H_4CH_2{-}NHC_6H_4R'$.[594] Phenylisocyanate is also reduced[589], but the products have not been reported. The C≡N bond takes up twice the quantity of hydrogen, so that nitriles RCN are reduced to amines RCH_2NH_2.[442] The reaction is said to proceed via RCH_2NBH[579], which is incidentally probably trimeric. Phenyl isocyanate also consumes more than two atoms of hydrogen.[589]

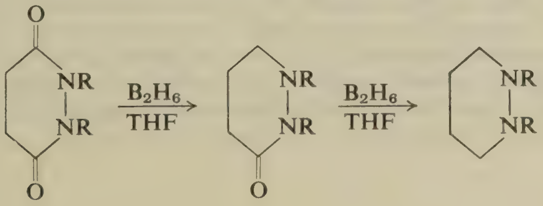
Bond cleavage occurs of necessity when the reduction takes place at a single bond. Aliphatic C—C bonds are not normally affected, but an exception is provided by cyclopropanes[595], in which the bonds are weakened through steric strain. With cyclohexane, cleavage occurs only under extreme conditions and in the presence of a catalyst.[596] The C—O bonds of ethers may also be cleaved at varying rates. Again strain may be largely responsible for the more facile reductive cleavage of a C—O bond in epoxides[579, 589, 597–8], which is catalyzed by small amounts of tetrahydroborate[599] or BF_3.[600] Tetrahydrofuran[601] and other cyclic ethers[602] are cleaved very much more slowly or require higher temperatures. With the former, diborane is said to react completely in 16 weeks at room temperature or 64 h at 60°C. At 80°C diisopropyl ether is also cleaved.[603] But, in general, dialkyl ethers show considerable resistance to reductive cleavage at room temperature, which enables them to be classed as useful solvents for diborane. However, some caution must be exercised, because a slow reaction is feasible, and such has been noted even with diglyme[604, 195], which, although one of the most commonly used solvents for diborane, has been observed slowly to liberate CH_4 as one of the products. Nevertheless, in accordance with one suggestion[222], all these cases of slow ether cleavage may be attributable to the catalytic effect of traces of boron trifluoride. There is still uncertainty concerning this point, but in no case has it been definitely established that B_2H_6 reacts in this way when completely free of BF_3.

Reductive cleavage is readily effected of one of the C—O bonds in acetals and ketals, which are thereby converted by diborane to ethers[605]:

$$RR'C(OR'')_2 \xrightarrow[(B_2H_6)]{[2H]} RR'CHOR''+R''OH$$

Most C—S bonds are not attacked, but reductive cleavage occurs in the cases of the triphenylmethyl mercaptan Ph_3CSH and disulphide $Ph_3CSSCPh_3$ to produce triphenylmethane.[606] The presence of the aryl groups seems to be necessary for such a reaction. Again, although C—Cl and C—Br bonds are normally assumed not to be attacked, aralkyl halides are reduced by reductive cleavage of the carbon-halogen bond, at least in nitromethane as solvent.[607] Diborane(6) has also been observed to cleave Si—C, Si—O and Si—P bonds with the production of silanes in the cases of silyl cyanide H_3SiCN[608], disiloxane (disilyl ether) $H_3SiOSiH_3$[609] and dialkylphosphinosilanes R'_3SiPR_2[610] respectively. Likewise stannanes have been produced with the cleavage of Sn—N[611] and Sn—O[612] bonds. The N—N bond, though normally not attacked, can be cleaved in benzoylhydrazines with the formation of amines by diborane in tetrahydrofuran.[613] The N=N double bond in azo compounds is similarly ruptured by diborane(6)[442], as is the N—O bond in hydroxylamines[593]; azoxybenzene, however, is not attacked.[590]

Reductions of the second class, in which an oxygen atom is extracted, have received very little study as yet: but a few clear cases are known in the almost quantitative conversion by diborane of triphenylphosphine oxide Ph_3PO and tris(dimethylamino)phosphine oxide $(Me_2N)_3PO$ to the corresponding phosphines, Ph_3P[614] and $(Me_2N)_3P$[615] respectively. The conversion of 1,2-substituted perhydropyridazin-3,6-diones to the corresponding perhydropyridazin-3-ones and eventually to the completely reduced perhydropyridazines by diborane in tetrahydrofuran[613] is strictly of the third class:



An oxygen atom is formally lost in the conversion by diborane of a tert-cyclopropylcarbinol $RCMe(C_3H_5)OH$ to the hydrocarbon $RCHMeC_3H_5$[221], but this is better regarded as a rare replacement of —OH by —H. Normally alcohols are not reduced by diborane, and even in this case catalysis by BF_3 is required.

In reductions of the third class, features of both of the first two classes appear. As stated above, ordinary aldehydes and ketones are reduced to alcohols; but if the compound is aromatic and exceptionally electron-rich the ultimate product is the substituted hydrocarbon.[587–8] Likewise fluoroacetamides are reduced to fluoroethylamines[616], although here the effect of the fluorine substituent is electron-withdrawing. The overall effect is the loss of an oxygen atom and the gain of two hydrogen atoms (although again this does not occur at a single step). Xanthones[617] behave like ordinary ketones towards diborane, as do cyclopropylketones[221] and lactones[586] in the presence of BF_3. With coumarins both hydrogenolysis of the carbonyl group and cleavage of the heterocyclic ring occur, so that coumarin itself gives *o*-allylphenol[222], this being an example of the gain of four hydrogen atoms and loss of one oxygen atom. With analogues, however, the degree of reduction may differ.[222, 618]

Carboxylic acids and their esters, but not their salts, react in stages to produce alcohols, the acids more rapidly and the esters more sluggishly than do ketones, so that under controlled conditions reduction of compounds with more than one functional group can be selective[250, 398, 619–20]: the reduction of the free acids can proceed via a triacylborane $(RCOO)_3B$[579, 621], and more than one subsequent pathway is conceivable.[622] Steric hindrance by the attached group may effect the reducibility of the carboxyl function, as has been observed, for example, with polycarbonate esters.[623] Treatment with diborane is an effective method for reducing carbohydrate carboxylic acids[624] and compounds of high molecular weight, such as carboxyl-terminated polysiloxanes[625], or peptides and proteins[626], where again a very valuable high selectivity is achieved by working at −10°C. An exactly comparable reaction occurs with certain substituted amides, so that, for example, N,N-dimethylformamide is reduced to trimethylamine[627]:

$$HCONMe_2 \xrightarrow[0°C]{B_2H_6} Me_3N.BH_3$$

However, with a limited quantity of B_2H_6 at −30°C, a product can be isolated that is apparently the adduct $HCOMe_2N.BH_3$, which explodes on warming to room temperature. Similarly N,N-dimethylacetamide is reduced to $Me_2EtN.BH_3$.

In their behaviour towards diborane, N=O bonds are sometimes completely reduced. Thus aromatic nitroso compounds[628] are reduced to amines. Alkyl nitro compounds however, do not react as such[589], but their salts (nitronates)[629] are reduced to N-monosubstituted hydroxylamines. The last reaction may be more correctly regarded as a combination of the first and second types of reduction, in that the incoming hydrogen atoms do not take the place of the oxygen atom removed and the loss of the oxygen atom is associated with the reduction in valency of the nitrogen atom, while the remaining nitrogen–oxygen bond is reduced and gives the —NHOH group. When pyridine N-oxide is reduced by diborane, the nitrogen is likewise brought to the trivalent state.[589]

In the fourth class of reduction by diborane, the outgoing atom or group is univalent, but a process more complex than reductive cleavage is involved. Thus three atoms of hydrogen are taken up in the reduction of oxime ethers $RR'C{=}NOR''$[593], when the observed products are amines plus alcohols. Still more hydrogen is required in the reduction of oxime esters $RR'C{=}NOCOR'''$[593, 630–1], to give the same products, but this is perhaps best regarded as a combination of the third and fourth classes of reduction, in that the acyl group is reduced to an alkoxy group during the process in a typically class-3 manner. Formally, at least, the conversion by diborane of benzoyl chloride and other acid chlorides[632–3] to the corresponding alcohol may be regarded as another example of a class-4 reduction, but it may also be regarded as a combination of classes 1 and 3. The versatility of diborane as a reducing agent is thus amply demonstrated.

A useful comparison has been made of the rates of reduction of a large number of functional groups by diborane under standard conditions.[589]

Hydroboration of Multiple Carbon-Carbon Bonds

Of outstanding importance is the behaviour of diborane(6) with ethylenic and acetylenic bonds. Although early experiments[634] showed that excess ethylene would react with B_2H_6 to give triethylborane,

$$B_2H_6 + 3C_2H_4 \rightarrow 2B(C_2H_5)_3$$

the inconvenience and slowness of the reaction, which requires 4 days at 100°C, caused its importance to remain unrecognized for several years. It was later found that this reaction is highly exothermic, can be catalyzed by active carbon or oxides such as Al_2O_3[635], and, with higher proportions of B_2H_6, can proceed explosively. The kinetics and mechanisms of the B_2H_6-C_2H_4 reaction are complex, although attempts have been made to interpret them.[636–7] The last stage of the reaction, at least, is reversible

$$BEt_3 \rightleftharpoons BHEt_2 + C_2H_4$$

with an activation energy which is as high as $33{\cdot}7 \pm 1{\cdot}2$ kcal mol^{-1} [638], but still much less than one-third of the energy required for complete dissociation to $B_2H_6 + 3C_2H_4$, namely $172{\cdot}5 \pm 2{\cdot}1$ kcal mol^{-1}.[639]

The observation reported in 1956 by H. C. Brown that olefins are readily converted into organoboranes at room temperature by the combined action of $NaBH_4$ and $AlCl_3$[640] soon led him to reinvestigate the action of B_2H_6[641] and make the historic discovery that, in the presence of ethers, diborane(6) adds very smoothly and rapidly to olefins at room temperature to produce organoboranes in nearly quantitative yields in an easily controllable reaction, for which the name 'hydroboration' was coined. Subsequently protonolysis by a carboxylic acid yields the saturated hydrocarbon[642]:

$$6RCH{=}CH_2 + B_2H_6 \rightarrow 2(RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B \xrightarrow{EtCOOH} 3RCH_2CH_3$$

The last stage is completed by refluxing in a high-boiling polyether solvent. Alternatively the saturated alcohol may be obtained as the final product—without necessarily isolating the intermediate—on oxidation by alkaline hydrogen peroxide[643–4]:

$$(RCH_2CH_2)_3B \xrightarrow{NaOH,\ H_2O_2} 3RCH_2CH_2OH$$

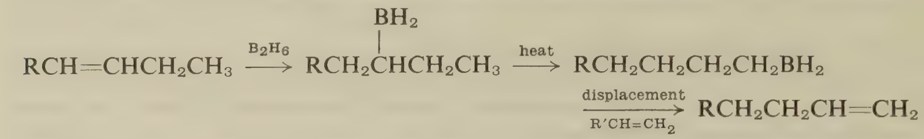
The type of addition across the double bond is *cis* and anti-Markownikoff, and is generally highly stereospecific.

Though in general a stream of gaseous diborane gives the best yields, it is frequently adequate to prepare the latter reagent *in situ*[644–5], e.g. from $NaBH_4$ and either BF_3 etherate or $AlCl_3$:

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3.OEt_2 \rightarrow 4(RCH_2{-}CH_2)_3B + 3NaBF_4 + 4Et_2O$$

$$9RCH{=}CH_2 + 3NaBH_4 + AlCl_3 \rightarrow 3(RCH_2{-}CH_2)_3B + 3NaCl + AlH_3$$

Quick recognition of the importance of the hydroboration reaction as a synthetic tool resulted in its intensive study. The reaction is general, but proceeds less rapidly with internal than with terminal double bonds. With the latter the boryl group attaches itself predominantly to the terminal carbon atom, and with the former the less sterically hindered position is favoured. Induction effects also play a role: thus boryl addition to styrene is 80% terminal, which figure rises to 93% with *p*-methoxystyrene, but drops to 65% with the *p*-chloro compound. By using partially substituted boranes in place of B_2H_6 these percentages may be modified, usually enhancing the directive effect, especially when the substituent is bulky. Such bulky groups may prevent the hydroboration from proceeding beyond the disubstituted or even monosubstituted borane stage. The monosubstituted compounds are normally dimers and hence derivatives of diborane. When the boron is not linked to a terminal carbon atom, isomerization, in which the boron migrates to the least sterically hindered position, occurs on heating. Since the olefin is subject to displacement by another olefin of greater reactivity, this effectively shifts the double bond and even enables olefins to be isomerized in a direction opposed to the order of increasing thermodynamic stability:

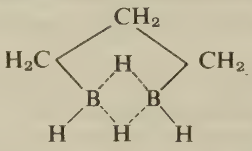


$$RCH{=}CHCH_2CH_3 \xrightarrow{B_2H_6} RCH_2\overset{BH_2}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{heat} RCH_2CH_2CH_2CH_2BH_2 \xrightarrow[R'CH=CH_2]{displacement} RCH_2CH_2CH{=}CH_2$$

Chain doubling through coupling occurs on application of alkaline silver nitrate, while ring closure occurs when chloro-olefins are hydroborated: thus allyl chloride gives cyclopropane, which, however, may itself be attacked by diborane (p. 101).[595]

The extreme versatility and serviceability of the hydroboration reaction, its stereochemistry and the influence of steric hindrance, isomerization, displacement, directive effects, selectivity and relative stabilities of functional groups towards reduction during hydroboration were all well understood by the latter part of 1961, when the earlier work was summarized in a book.[500]

Dienes normally give diols after treatment of the initial products, which, as produced in ether solution, are not simple but polymeric and of low volatility. However, if the diene is conjugated it is less reactive, while aromatic rings are completely unreactive. With conjugated dienes the unsaturated monohydric alcohol is not produced by partial hydroboration, because the second C=C double bond is attacked much faster than the first. At higher temperatures and in the absence of ether, or after thermal rearrangement, the products may be simple, so that a bora- and a bis-bora-cyclylalkane can be obtained as volatile liquids from butadiene and diborane.[494, 646] The mechanism of the butadiene reaction has received study.[647] Allene is peculiar in giving initially the cyclic compound 1,2-trimethylenediborane(6)[492]



which undergoes a rapid and reversible polymerization.

Acetylenes hydroborate very rapidly and also initially give non-volatile products. The C≡C triple bond is capable of bis-hydroboration. Thus 1-hexyne gives a polymeric diborylhexane containing the two boryl groups for the most part attached to the same terminal carbon atom, i.e. predominantly $H_3C(CH_2)_4CH(BH_2)_2$.[648] This on further treatment gives largely 1-hexanol, a fact attributed to the rapid hydrolysis of one of the boron-carbon bonds. However, it must be remembered that if an aldehyde were formed it would be immediately reduced to the alcohol by the boranes still present. Under other conditions terminal acetylenes give mainly aldehydes, while internal acetylenes give ketones.[649] Monohydroboration of the triple bond is also feasible, when vinylboranes and thence *cis*-olefins are produced.[649] Treatment of the vinylboranes with iodine can lead to interesting transfer reactions.[650] Acetylene itself is unusual and gives with diborane a polymer of formula $[B_2(C_2H_4)_3]_n$[651]: this yields mainly ethane on hydrolysis with propionic acid.

Recent advances in hydroboration applications include the use of carbon monoxide. At or above 100°C with an organoborane such as triethylborane(3) in diglyme, this will give rise to a product which, upon the usual oxidation, yields a tertiary alcohol[652]: but in the presence of water the product is a ketone.[653]

$$R_3B + CO \xrightarrow[\text{diglyme}]{100^\circ\text{–}125^\circ C} [R_3CBO] \xrightarrow{NaOH,\ H_2O_2} R_3COH$$

$$R_3B + CO \xrightarrow[H_2O]{100^\circ C} RB(OH)CR_2OH \xrightarrow{NaOH,\ H_2O_2} R_2CO$$

In these examples the chain length is more than doubled by the transfer of alkyl groups to the carbonyl carbon atom. Under different conditions, by using carbon monoxide in conjunction with $NaBH_4$ or $LiAlH(OMe)_3$ at lower temperatures, primary alcohols[654] or aldehydes[655] are produced and the chain length is increased by one carbon atom only:

$$R_3B + CO \xrightarrow[\text{NaBH}_4\text{, diglyme}]{45^\circ\text{C}} \xrightarrow{\text{KOH}} RCH_2OH$$

$$R_3B + CO \xrightarrow[\text{LiAlH(OMe)}_3\text{, THF}]{25^\circ\text{C}} \xrightarrow[\text{buffer}]{H_2O_2} 2ROH + RCHO$$

Carbon monoxide in the presence of other reagents will also give carboxylic acids[656] with the products of hydroboration.

The chain length has been increased by more than one carbon atom at a time in a hydroboration procedure which uses unsaturated ketones and aldehydes to prepare higher saturated ketones[657] and alcohols[658], and in other methods which use ethyl bromoacetate or chloracetonitrile to produce an ester[659] or a nitrile[660] respectively. Such procedures have considerable potential synthetic value. Instead of diborane(6), many of its derivatives and also certain borane(3) adducts have been used in hydroboration procedures, including $R_3N.BH_3$ and $R_3N.BH_2Cl$.[661]

Concerning the hydroboration of multiple bonds involving elements other than carbon, see p. 100.

REACTIONS WITH HYDROGEN AND ITS COMPOUNDS

Diborane(6) does not react with elemental hydrogen, except to undergo hydrogen exchange (p. 138). Indeed, hydrogen tends to stabilize diborane(6), apparently because of the reversibility of the decomposition step[18]

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

With metal hydrides like LiH, NaH or KH, tetrahydroborates are formed; but such reactions will in general only proceed satisfactorily, if at all, in the presence of a solvent suitable for the product[218, 662–3]:

$$NaH \xrightarrow[\text{diglyme}]{\frac{1}{2}B_2H_6} NaBH_4 \xrightarrow[\text{diglyme}]{\frac{1}{2}B_2H_6} NaB_2H_7 \text{ (solvated)} \xrightarrow[\substack{100^\circ\text{C}\\ \text{diglyme}}]{\frac{1}{2}B_2H_6} NaB_3H_8 + H_2$$

The heptahydrodiborate(1−) NaB_2H_7 cannot be freed from solvent without decomposition. The conditions under which the reaction with NaH proceeds further to give salts of the $B_3H_8^-$ and $B_{12}H_{12}^{2-}$ anions have been studied.[664] The reaction of diborane(6) with BeH_2 gives BeB_2H_8 and requires warming[665], but reactions with MgH_2[666–7] and CaH_2[668] require the presence of an ether, e.g. tetrahydrofuran or diethyl ether, and, with advantage, pressure:

$$MgH_2 \xrightarrow[\substack{C_4H_8O\\ \text{or } Et_2O}]{B_2H_6} Mg(BH_4)_2 \xrightarrow[100^\circ\text{C}]{2B_2H_6} Mg(B_3H_8)_2 + 2H_2 \rightarrow \text{higher hydropolyborates}$$

Diborane reacts with a number of other hydrides of boron. Diborane(4) B_2H_4 is not isolable, but the isolable adduct $B_2H_4(PF_3)_2$ is converted almost quantitatively into tetraborane[36–7]:

$$B_2H_4(PF_3)_2 + B_2H_6 \rightarrow B_4H_{10} + 2PF_3$$

With other boron hydrides, diborane(6) may undergo exchange of BH_3 groups at a measurable rate[669] if the second borane is hydrogen-rich, i.e. contains a BH_2 terminal group. These include B_4H_{10} and B_5H_{11}, but not B_5H_9, B_6H_{10} or $B_{10}H_{14}$, with which species only hydrogen exchange can occur.[669] Otherwise, especially on heating, chemical reaction leading to higher boranes takes place. Thus B_4H_{10} is largely converted initially into B_5H_{11}[670–2], while B_5H_{11} is converted to n-B_9H_{15}[17] and other products.[367] On the other hand, diborane(6) converts B_5H_9 on co-pyrolysis mainly to $B_{10}H_{14}$ and a solid polymer, $(BH)_x$, though probably not by direct action[18], since it has been shown that just one-half of the boron of the $B_{10}H_{14}$ comes from the B_2H_6.[348] Rather, it has been reported that this reaction is complex and that smaller amounts of many other products occur.[673] Diborane(6) will convert $B_{10}H_{14}$ to a non-volatile polymeric boron hydride[350], but the reaction is slow and again does not occur directly, but in all probability by the interaction of $B_{10}H_{14}$ with pyrolysis products of B_2H_6.[18] With the tetraborane(8) adducts B_4H_8CO or $B_4H_8PF_3$, diborane(6) will give B_4H_{10} and B_5H_{11}, which may thus be prepared in an isotopically labelled form.[674] With ionic species B_2H_6 may undergo boron exchange, as with $NaB_{10}H_{13}$[675], or effect complete chemical change. Thus, according to the conditions, the tetrahydroborate(1−) ion BH_4^- is converted either to $B_2H_7^-$[387, 234] or via $B_3H_8^-$ to the $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$ ions.[676] The presence of an ether as solvent appears to be necessary. The conversion of the sodium salt $NaBH_4$ in diglyme at 100°C to the octahydrotriborate(1−) NaB_3H_8 by iodine[677] is doubtless best regarded as the result of action by B_2H_6 prepared *in situ*, for diborane(6) is first liberated by the action of I_2 on $NaBH_4$[264]:

$$2NaBH_4 + I_2 \xrightarrow[25°C]{\text{diglyme}} 2NaI + B_2H_6 + H_2$$

$$BH_4^- + B_2H_6 \xrightarrow[100°C]{\text{diglyme}} B_3H_8^- + H_2$$

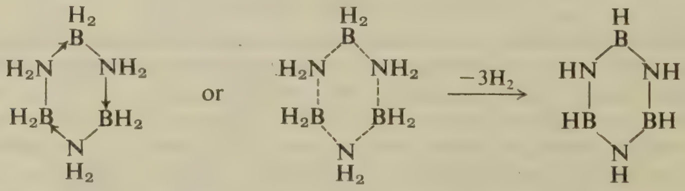
In ether solution the aluminium hydrides AlH_3[678] and $LiAlH_4$ or $NaAlH_4$[679] are converted by diborane(6) via the partially substituted hydrides AlH_2BH_4 and $AlH(BH_4)_2$ to aluminium tetrahydroborate $Al(BH_4)_3$. It is possible that species of the type $Li[AlH_{4-n}(BH_4)_n]$ are intermediates.[439, 680] The final result may even be salts of the complex anion $[Al(BH_4)_4]^-$, as has been observed with the tetraalkylammonium aluminium hydrides at 20°–60°C[681–2]:

$$[NR_4]AlH_4 + 2B_2H_6 \rightarrow [NR_4][Al(BH_4)_4]$$

Alkoxyaluminium hydrides $[(RO)_nAlH_{3-n}]_x$ are however converted by diborane(6) to alkoxyaluminium tetrahydroborates.[683] Uranium hydride UH_3 on heating in diborane(6) yields uranium boride.[684]

With saturated hydrocarbons, B_2H_6 reacts to a negligible extent below 100°C, but at temperatures at which its pyrolysis becomes rapid (180°C) significant carbon-carbon bond rupture and boron-carbon bond formation occurs.[634] In the presence of a Friedel–Crafts catalyst, other reactions may occur.[596] With cyclopropanes the cleavage of a C—C bond occurs more readily and leads to the formation of primary alkyl substitution at the boron.[685, 595] Because of the general inertness of C—H bonds towards diborane(6) at room temperature, however, B_2H_6 can be used for the manometric determination of active hydrogen in organic compounds.[686] Unsaturated hydrocarbons are immediately attacked at the multiple bond in an addition reaction which involves the cleavage of one or more B—H bonds on each boron atom of the diborane(6), and an account of this important reaction, i.e. hydroboration, is given on p. 103. Diborane(6) would not be expected to react readily with the lowest hydrides of other group-IV elements, but detailed studies do not appear to have been undertaken.

With the hydrides of group-V elements, the initial reaction is addition or substitution as already described on pp. 85, 86 and 91, respectively. Especially at higher temperatures, borazine $B_3N_3H_6$ is formed by diborane(6) with ammonia by condensation, hydrogen-elimination and ring-closure reactions[320]:



boranamine cyclic trimer   borazine

In its formation, the trimeric boranamine (cyclotriborazane), known from other reactions, is a likely intermediate. With excess ammonia and at progressively higher temperatures, borimide $B_2(NH)_3$ and boron nitride BN are among the products.[687] Apart from giving adducts (p. 24), hydrazine reacts with diborane with the liberation of hydrogen.[688] Diphosphine P_2H_4 reacts with B_2H_6 to give the bis-borane(3) adduct $P_2H_4.2BH_3$.[689]

Of the reactions with the hydrides of group-VI elements, that with water is a special case, in that it leads to the complete decomposition of diborane(6) at room temperature without the formation of isolable intermediates (see p. 123). With liquid H_2S, diborane(6) furnishes no evidence for adduct formation or thiohydrolysis, and has not more than a slight tendency to form ions under neutral conditions; but in the presence of a base, e.g. with thio analogues such as $Me_4N^+SH^-$, diborane(6) first forms the ion $[HS(BH_3)_2]^-$.[690] The resultant solution is unstable and readily loses hydrogen to give unidentified products, which could feasibly include the more recently discovered μ-mercaptodiborane[557] described on p. 97. With gaseous H_2S at room temperature, B_2H_6 slowly gives a polymer of composition $(HBS)_x$.[395] Its reactions with higher hydrides of sulphur and with H_2Se and H_2Te appear not to have received study.

Likewise the reaction of B_2H_6 with HF appears not to have been investigated, but because of the unusually high affinity of boron for fluorine, hydrogen could be expected to be ejected rather readily with the formation of BHF_2 or BF_3. With the other hydrogen halides the product is the monohalogenodiborane(6) B_2H_5X, but in the cases of HCl and HBr the reaction is inconveniently slow, though with HBr it can be catalyzed by aluminium bromide[320] (p. 98).

REACTIONS WITH METALS AND THEIR COMPOUNDS

Since the behaviour of diborane(6) with metals is of particular interest, it is curious that, of the more electropositive metals, only sodium, potassium and calcium have been investigated in their reactions with diborane(6). The B_2H_6 is slowly absorbed, but the reaction requires several days to complete, even if the metal is amalgamated. At the time of the earliest studies[691–3], tetrahydroborates were not known, and the products were assumed to be salts of the type $Na_2[B_2H_6]$, $K_2[B_2H_6]$ and $Ca[B_2H_6]$, in which there was supposed to be a hexahydrodiborate(2−) ion $B_2H_6^{2-}$, isostructural with ethane. After sublimation, the crystalline product from the potassium reaction was observed to be cubic with a single refractive index.[694] Had it been noted that this implied either an incorrect formula or that the substance underwent change on sublimation, the tetrahydroborate(1−) ion BH_4^- might have been identified about a decade earlier than it was. It was not until 1949 that the X-ray powder-diffraction pattern of the product from the sodium-diborane reaction was shown to be identical with that of sodium tetrahydroborate $NaBH_4$[695], which had meanwhile been prepared by other methods. Although this is generally assumed to settle the matter, it must be pointed out that the product had been heated during the sublimation process, so that there is still no rigid proof that the earlier conclusions were wrong and that the hexahydrodiborate(2−) $Na_2[B_2H_6]$ or some comparable intermediate is not first formed at room temperature. Unlike potassium tetrahydroborate(1−) KBH_4[696], the original product of the potassium-diborane reaction is reported to be insoluble in liquid ammonia[692] and only partly sublimable[693], so that the reaction in the absence of solvent needs further study. In any case, some rearrangement must occur to account for the transfer of a fourth hydrogen atom to the boron atom.

A third substance may speed up the reaction. In the presence of an ether as solvent the above rearrangement is favoured at room temperature and the whole reaction greatly accelerated. The overall reaction with sodium amalgam has been demonstrated to involve the simultaneous formation of the octahydrotriborate(1−)[697–8]:

$$2Na + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8$$

Even here, however, there is evidence for the formation of intermediates, kinetic data being consistent with the initial formation of $Na_2B_2H_6$, which reacts further with diborane(6) to give NaB_2H_6 or $Na_2B_4H_{12}$ as a second intermediate with its own characteristic X-ray diffraction pattern distinct from those of $NaBH_4$ and NaB_3H_8, into which compounds it decomposes with time.

The reaction of B_2H_6 with lithium, either in the presence or absence of a solvent, remains unreported. This omission would be worth rectifying, since especially with compounds of the lighter elements the reactions of lithium often differ from those of sodium and potassium.

In place of sodium amalgam, the addition compounds of sodium with naphthalene or triphenylborane(3) react with B_2H_6 in ether to give the same products.[699] The much higher speed of reaction is a major advantage. Dissolved in liquid ammonia, sodium apparently does not react in an identical way, but gives a variety of products in a complex reaction.[388]

It has been claimed[700] that if a cyclic ether is used as solvent, alkaline-earth metals and aluminium in the form of their amalgams will react with diborane(6) in a manner comparable to alkali metals. So far as is known, transition metals do not react with B_2H_6, but finely divided metals such as nickel or platinum will catalyze its decomposition at room temperature.[701]

The reaction of diborane(6) with metal compounds has received but limited study. However, its action on carbonyl anions of metals in the manganese and cobalt vertical groups has been investigated (see p. 88). With trinitrosylcobalt $Co(NO)_3$ it apparently gives $(ON)_3Co.BH_3$[702], comparable with the better characterized $(ON)_3Co.BMe_3$. Its direct action on metal cyclopentadienyls has not been reported, but there is no obvious reason why such compounds as ferrocenylborane should not be obtainable, since other starting materials provide derivatives.[703–4] Reaction of diborane(6) with many metal hydrides (see p. 114) and with several metal alkyls has received attention, but, surprisingly, not that with the alkyls of the more electropositive metals Na, K, Ca, Sr or Ba. Ethyllithium gives the tetrahydroborate and alkyldiboranes, e.g.[248]:

$$2LiEt + 2B_2H_6 \rightarrow 2LiBH_4 + B_2H_4Et_2$$

Methyllithium behaves in a like manner[705], but phenyllithium may react differently. One group of workers states that it gives the phenyltrihydroborate(1−)[706]

$$2LiPh + B_2H_6 \rightarrow 2LiBH_3Ph$$

but elsewhere it is stated to give first phenyldiborane(6), which reacts further[705]

$$B_2H_6 \xrightarrow{\text{LiPh}} B_2H_5Ph \underset{}{\overset{\text{LiPh}}{\rightleftarrows}} PhBH_2$$

Dimethylberyllium and trimethylaluminium resemble methyllithium and give, ultimately, BeB_2H_8[707–8] and $Al(BH_4)_3$[709] respectively, which, however, unlike $LiBH_4$, are strictly covalent. The reaction of B_2H_6 with dimethylberyllium $BeMe_2$ proceeds in at least four stages, giving first a glassy material, second a still methyl-rich non-volatile mobile liquid, and third the volatile and fully characterized intermediate $MeBeBH_4$[707–8]; the BeB_2H_8 only appears at a subsequent final stage. Diethylmagnesium can give $Mg(BH_4)_2$, but the reaction is complex unless a trialkylaluminium is present in catalytic amounts[710]; in its absence a variety of products result, including $EtMgBH_3Et$ and $Mg(BH_3Et)_2$ as well as MgH_2.[711–13] Grignard reagents RMgX in tetrahydrofuran were originally reported to give compounds of general formula $HMgX.2C_4H_8O$ with diborane(6)[714], but other workers were unable to repeat this and obtained instead the tetrahydrofuran adduct $XMgBH_4.2C_4H_8O$ with traces of alkyl-substituted ions such as BH_3R^- and $BH_2R_2^-$.[715–16] Trimethylgallium gives $Ga(BH_4)_3$ at reduced temperatures[717], but at room temperature this is liable to decompose to the metal by an autocatalytic reaction. The product with $InMe_3$ is even less stable.[718] Diborane(6) does not react with trimethylstannane $SnHMe_3$, except to catalyze its decomposition to Sn_2Me_6 and $(SnMe_2)_n$.[719] Organolead compounds such as tetramethyl-[478] and tetravinyl-lead[479], on the other hand, do react, but in a manner differing from the foregoing cases: the end products are metallic lead and the organoborane(3):

$$3PbR_4 + 2B_2H_6 \rightarrow 3Pb + 4BR_3 + 6H_2$$

Diborane(6) reacts with certain alkoxides in ether solution to form tetrahydroborates, with the transference of alkoxy groups to the boron. Potassium methoxide does not react, but alkoxides of lithium and sodium such as LiOEt and NaOMe do so readily[720, 218]:

$$3NaOMe + 2B_2H_6 \rightarrow 3NaBH_4 + B(OMe)_3$$

Alkaline-earth metal ethoxides also react.[721] Such reactions may produce new kinds of tetrahydroborates, even at low temperatures, as occurs with alkoxy derivatives of aluminium[302], tin(II)[722] and lead(IV)[723]:

$$4Al(OCHMe_2)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3.3Al(OCHMe_2)_3 + B(OCHMe_2)_3$$

$$2Sn(OMe)_2 + 3B_2H_6 \rightarrow 2Sn(BH_4)_2 + 2BH(OMe)_2$$

$$4R_3PbOMe + 3B_2H_6 \rightarrow 4R_3PbBH_4 + 2BH(OMe)_2$$

The stability of the products varies widely: for example $Sn(BH_4)_2$ decomposes to the metal above −65°C. Tin(IV) alkoxides react differently and give stannane or the corresponding substituted stannane[612]:

$$Sn(OMe)_4 + B_2H_6 \rightarrow SnH_4 + 2BH(OMe)_2$$

$$4R_3SnOMe + B_2H_6 \rightarrow 4R_3SnH + 2BH(OMe)_2$$

The alkoxides $Ti(OBu)_4$ and $Zr(OCHMe_2)_4$ in tetrahydrofuran, however, give the tetrahydroborates $Ti(BH_4)_3$ and $Zr(BH_4)_4$ respectively[724], as would be expected of transition metals. With metal dialkylamides the dialkylamino group is likewise transferred to boron, at least in the case of tin(IV) compounds, but again stannanes and not tetrahydroborates result[611]

$$2R_{4-n}Sn(NEt_2)_n + nB_2H_6 \rightarrow 2R_{4-n}SnH_n + 2nH_2BNEt_2$$

With metal salts, two possible courses of reaction arise, in that either the cation or the anion may be attacked by diborane(6). The cation may be involved when the metal is noble in character, so that acidified cupric sulphate is reduced at 0°C mainly to copper hydride CuH with some crystalline copper[725]; or, presumably, when a metal of variable valency can be reduced to a lower valence state. Surprisingly, further evidence on the latter point is lacking, both for crystalline salts and their solutions: the case mentioned above of the conversion of titanium(IV) butoxide $Ti(OBu)_4$ to a Ti(III) compound hardly refers to a salt. For salts of strongly electropositive metals such as sodium, or even magnesium, the only possibility of reaction is with the anion, and such is liable to occur when, for example, the free ion can add on a BH_3 unit. Several examples of this are cited on p. 87. The reaction does not always stop at the addition stage, however. Thus $NaBH_4$ dissolved in diglyme is converted to NaB_2H_7[234], but at higher temperatures the product is NaB_3H_8[726] with liberation of hydrogen. The reaction with B_2H_6 proceeds differently with alkoxy and amino derivatives such as $Na[B(OMe)_4]$[727], $Mg[B(OR)_4]_2$[728], $Na[BH(OMe)_3]$[218] or $K[H_2NBMe_3]$[729], for which group replacement is observed:

$$3NaB(OMe)_4 + 2B_2H_6 \rightarrow 3NaBH_4 + 4B(OMe)_3$$

$$2NaBH(OMe)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OMe)_3$$

$$2K[H_2NBMe_3] + 3B_2H_6 \rightarrow 2K[H_2N.B_2H_6] + 2B_2H_3Me_3$$

It is however probably more correct to regard the product written as $K[H_2N.B_2H_6]$ as a mixture of KBH_4 and polymeric H_2NBH_2.[729] With sodium azide NaN_3 in ether, B_2H_6 gives $NaBH_4$ and azidoborane H_2BN_3.[445] With aqueous NaOH the product is likewise mainly $NaBH_4$.[730] That the last reaction is to be regarded as a reaction of the OH^- ion, is clear from the fact that $[Me_4N]OH$ reacts in a similar way in solution to give Me_4NBH_4. With phosphomolybdic acid a blue coloration of unknown origin is obtained, and this may be used as the basis of a method for determining diborane(6).[731]

The reactions of B_2H_6 with metal complexes other than the carbonyls mentioned above have been little studied. However, it has been briefly reported that the bis-1,10-phenanthroline complex of ferrous cyanide, $Fe(C_{12}H_8N_2)_2(CN)_2$, forms the adduct $Fe(C_{12}H_8N_2)_2(CN)_2.2BH_3$, in which it is believed that the BH_3 groups are linked to the nitrogen atoms of the cyano groups.[732]

REACTIONS WITH OTHER BORON COMPOUNDS

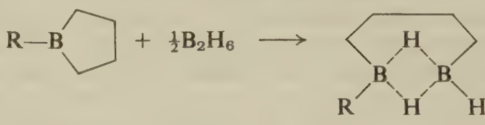
Diborane(6) frequently shows reactivity towards other compounds of boron. Several such reactions have already received mention, namely those with other boranes (pp. 138, 223) and with the tetrahydroborate(1−) ion (p. 87). The reversible redistribution reactions with trialkylboranes (p. 88), borate esters (p. 95), thioborates (p. 97) and boron trihalides (p. 98) have also been described. Relatively few additional reactions with other classes of boron compounds have been studied.

With substituted diboranes, diborane(6) may undergo isotope-exchange reactions, as with μ-(dimethylamino)diborane(6) $Me_2NB_2H_5$.[733] It reacts more radically with substituted tetrahydroborates, when one of the products is normally the unsubstituted tetrahydroborate[218, 728], and this may, of course, react further:

$$2NaBH(OMe)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OMe)_3$$

$$3Mg[B(OMe)_4]_2 + 4B_2H_6 \rightarrow 3Mg(BH_4)_2 + 8B(OMe)_3$$

Disodium dimethylhydroborate(2−) Na_2HBMe_2 also reacts with diborane(6), but in this case about 1·4 BH_3 groups per molecule are added to give a product stable *in vacuo* at 25°C and which apparently does not contain $NaBH_4$.[734] With some cyclic organic boranes, diborane(6) effects ring opening with the entry of a BH_3 group[735], e.g.



B-alkylborolane 1-alkyl-1,2-tetramethylenediborane(6)

With aminoborazines, diborane(6) reacts with cleavage of the exocyclic B—N bonds to give the corresponding borazines plus polymeric boron-nitrogen compounds and hydrogen.[736] Diborane(6) reacts with the gaseous species $H_2B_2O_3$ to give boroxine $H_3B_3O_3$ by a reaction which is photochemically accelerated[737]:

$$H_2B_2O_3 + \tfrac{1}{2}B_2H_6 \rightarrow H_3B_3O_3 + H_2$$

The borane(3) adducts of organic sulphides, when heated with diborane(6), react with the loss of hydrogen and yield polyboron compounds of unusual stability.[738] Diborane(6) reacts with diboron tetrachloride B_2Cl_4 in a complex reaction producing BCl_3 and viscous liquid products[318], but B_2H_5Cl, $BHCl_2$, an unidentified solid, and some hydrogen have also been reported.[578] In ether solution at −23°C the reaction is less complex, and apparently follows the course:

$$B_2Cl_4 \xrightarrow[Et_2O]{B_2H_6} \underset{\text{(in } Et_2O \text{ solution)}}{B_2Cl_4.B_2H_6} \xrightarrow[\text{excess } Et_2O]{\text{removal of}} B_3H_3Cl_4.2Et_2O$$

REACTIONS WITH CARBON COMPOUNDS

Of concern here are solely the reactions of diborane(6) that lead to boron-carbon bond formation. The number of carbon compounds which react additively with diborane(6) to form borane(3) adducts that have carbon directly linked to boron is small and confined to carbon monoxide (see p. 15) and isocyanides (p. 17), and to certain ylides. A boron-carbon bond is also present in the borane(3) adduct[449] and bis-borane(3) adduct[439] (p. 17) formed by the cyanide ion. With ylides a boron-carbon bond is formed if the ylide bond is between carbon and either phosphorus, arsenic or sulphur, as in $Ph_3\overset{+}{P}—\overset{-}{C}H_2$ or $Me_3\overset{+}{As}—\overset{-}{C}HSiMe_3$ (p. 120), or in $Me_2\overset{+}{S}—\overset{-}{C}HSiMe_3$ (p. 131). However, if the ylide bond is to nitrogen, as in $Me_3\overset{+}{N}—\overset{-}{C}H_2$, no comparable reaction occurs (p. 115).

Organically substituted boranes may be formed by reacting diborane(6) with certain organometalic compounds (pp. 89 and 108) and organic compounds containing multiple carbon-carbon bonds (p. 89). Only in the case of cyclopropanes are single carbon-carbon bonds known to react comparatively readily.[523, 685] A few other reactions lead to the formation of carboranes (p. 134). In other cases of reduction of organic compounds the products do not contain boron-carbon bonds (p. 125): this is in line with the preference of boron to attach itself to elements possessing lone pairs of electrons.

Because of the general inertness of C—H bonds towards diborane(6), there are virtually no reactions involving carbon which do not fall into one of the above classes. Excited molecules may react, as illustrated by the photolysis of hexafluoroacetone in the presence of diborane[356], but the products are ill-defined.

REACTIONS WITH COMPOUNDS OF SILICON AND GERMANIUM

Although compounds containing boron-silicon bonds are readily preparable from halogenated boranes[739], only in the cases of the ionic compounds $KSiH_3$[440] and $KGeH_3$[441] have there been reports of reactions of diborane(6) leading to products in which the boron is directly linked to silicon or germanium, and even these products are very unstable. The ultimate products with $KSiH_3$, for example, are mainly KBH_4, SiH_4 and the solid hydride $(SiH_2)_n$.[440, 460] In other cases where reaction occurs under controlled conditions—as with the silyl cyanides H_3SiCN and Me_3SiCN[608], the silylamines H_3SiNMe_2 and $(H_3Si)_2NMe$[740], the silylphosphines H_3SiPH_2[741] and $(H_3Si)_3P$[742–3], silylarsine H_3SiAsH_2[744], disilyl ether $(H_3Si)_2O$[609] and the germyl compounds H_3GePH_2[745] and H_3GeAsH_2[746]—the first products, although not always positively identified, appear invariably to be borane(3) adducts in which, as expected, the boron is linked as acceptor to the group-V or group-VI element, even though the adducts from both of the arsines cited are too unstable to isolate. The position is not always so simple, however, since redistribution of the silyl and germyl ligands about the group-V atoms may be promoted by the B_2H_6, so that, for example, H_3SiAsH_2 is converted partly to $(H_3Si)_3As$.[744] Also, isotope studies have shown that proton exchange occurs between the boron and the silicon or germanium respectively in silyl[747] and germyl compounds.[745–6] Under more vigorous conditions each of the above-mentioned silyl cyanides is reduced to the appropriate silane with the rupture of the silicon-cyanide bond.[608]

Attempts to react B_2H_6 with silyl isocyanate H_3SiNCO failed.[748]

REACTIONS WITH NITROGEN AND ITS COMPOUNDS

Diborane(6) is attacked by atomic nitrogen: the products have not been identified, but the wavelength and distribution of the light emitted have received study.[749] It does not however interact chemically with molecular nitrogen. No appreciable formation of boron nitride BN is to be expected or is observed, even when B_2H_6 is burnt in air under fuel-rich conditions[750], in contrast to the results observed if the nitrogen is initially present as hydrazine N_2H_4.

The chemical behaviour of diborane(6) with nitrogen compounds is strongly connected with the fact that boron forms rather strong bonds with nitrogen, which bonds are moreover of several different kinds and bond orders. First to be encountered are the dative bonds which can arise by virtue of the donor powers of a trivalent nitrogen atom and the acceptor powers of a boron atom, although the acceptor powers are much weaker in diborane(6) than in free BH_3, a fact to be associated with the reorganization that the B_2H_6 unit must undergo in order to provide a suitably oriented vacant orbital for accepting a lone pair of electrons. Except where steric or other effects interfere, such bonds are very readily formed, even at low temperatures. If both boron atoms in B_2H_6 act as acceptors the bridge bond between the boron atoms is dissolved symmetrically, but if only one boron atom becomes linked to a nitrogen atom a weakened form of the bridge bonding involving only one hydrogen atom may be preserved, as already noted on p. 84: a third possibility arises when two nitrogen atoms link up with the same boron atom and give rise to an ionic compound through asymmetric cleavage of the diborane.

Thus the reaction of diborane(6) with ammonia is exceedingly complex, giving rise under variously controlled conditions to $H_3N.B_2H_6$, $H_3N.BH_3$ or $[H_2B(NH_3)_2]^+[BH_4]^-$

cf. pp. 85, 18); but, as mentioned below, when hydrogen is lost yet many other products are formed, including boranamine in various states of aggregation and borazine. Even at very much reduced temperatures, the reaction of B_2H_6 with ammonia is remarkably dependent upon the experimental conditions.[529, 388] There is good evidence that the first product obtained from the controlled, slow addition of diborane(6) vapour to solid ammonia at about −120°C is $H_3N.B_2H_6$.[388] But if the product is maintained at −78°C for some time and the unreacted ammonia distilled away, a diammoniate of diborane remains which has the ionic structure $[BH_2(NH_3)_2][BH_4]$[388], a compound that can be more easily prepared by passing a stream of diborane(6) diluted with nitrogen into liquid ammonia at −78°C.[419] This, however, can be converted to the isomeric ammonia borane(3) $H_3N.BH_3$ (p. 18) by suspending it in ether and treating it, for example, with ammonium chloride[414–16], or, more efficiently, by allowing it to stand for several days in diglyme solution containing a trace of B_2H_6.[751] If the addition of the reactants is reversed and ammonia is passed into a solution of B_2H_6 in tetrahydrofuran at −78°C, the two isomers are produced in approximately equal quantities[419], and after evaporation of the solvent and excess ammonia the monomer $H_3N.BH_3$ can be extracted from the mixture by diethyl ether, in which the ionic dimer is insoluble.

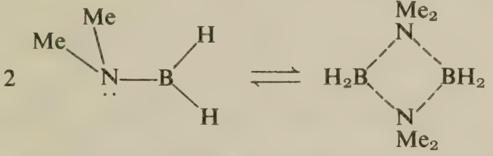
Normally heating is required to cause ammonia borane to lose hydrogen, but under the influence of tetrahydrofuran as solvent hydrogen evolution can occur even at reduced temperatures, since if the above tetrahydrofuran solution is first stored for some hours at −78°C and then allowed to warm to −10°C, an ammoniated form of a boranamine polymer $(BH_2NH_2)_n$ is precipitated.[752] At 100°C, B_2H_6 and ammonia will give hydrogen and polymeric boranamine direct.[517] Such polymers must be formed via the monomer BH_2NH_2, knowledge of which as a transitory species for a long time rested on evidence obtained from the pyrolysis of the dimer[530] and from a mass-spectrometric study of the vapour of subliming ammonia borane $H_3N.BH_3$[753] until the monomeric species was successfully trapped by cryochemical means.[754] The monomer begins to polymerize even below −155°C. In addition to amorphous polymers, the isolable forms of boranamines include a number of cyclic oligomers $(H_2NBH_2)_n$, where n may equal 2, 3, (4), 5, . . .[530] There has been an *ab initio* calculation of the structure and dissociation energy of the dimer.[755] For more information concerning the various forms of boranamine, see p. 423. As both the monomer and the ionic diammoniate of diborane $[BH_2(NH_3)_2][BH_4]$ can react with more B_2H_6 to give μ-aminodiborane(6) $H_2NB_2H_5$ (p. 91)[517, 516], this constitutes yet another compound formed from the interaction of diborane(6) and ammonia at 200°C[687], which at appropriate temperatures and in suitable concentrations may also give borazine $(BHNH)_3$, borimide $B_2(NH)_3$ and boron nitride BN. For the last, a temperature of about 400°C is required.[687]

Compared with the highly complicated behaviour of diborane(6) with ammonia, in its reactions with primary, secondary and tertiary amines the overall picture becomes progressively less complex[423] and is simplest in the case of tertiary amines NR_3, which readily give only borane(3) adducts $R_3N.BH_3$, although the rather precarious existence of the diborane(6) adducts $Me_3N.B_2H_6$[389] and $Et_3N.B_2H_6$[387] has been demonstrated. Indeed, the kinetics of formation of $Me_3N.BH_3$ from B_2H_6 and trimethylamine indicate that $Me_3N.B_2H_6$ is an essential intermediate.[756]

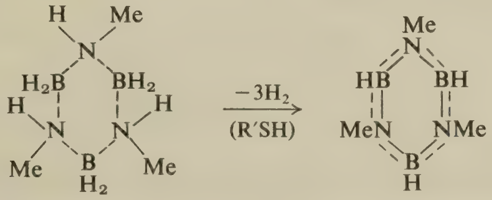
Instead of using gaseous diborane(6), amine boranes may be rapidly and efficiently prepared by treating the amine with $NaBH_4$ and iodine in monoglyme.[757] This is tantamount to preparing diborane(6) *in situ*, because B_2H_6 is known to be liberated almost quantitatively from $NaBH_4$ by iodine dissolved in a glyme.[264]

With the evolution of hydrogen on heating, amine boranes $HR_2N.BH_3$ and $H_2RN.BH_3$ give substituted boranamines[517] (pp. 424, 425), the former also borazines[533], and under some circumstances even salts of polyhedral borane anions (see below). For $HMe_2N.BH_3$ this hydrogen elimination has been shown not to be a unimolecular step.[758] With the conversion of amine boranes to boranamines, the B—N bond order is increased and the stretching force constant rises to *c.* 7·0 mdyne Å^{-1}, which is about double that for amine boranes, but sinks back somewhat in borazines.[759] Accordingly the calculated bond order of less than 0·7 obtained for the B—N bond in N,N-dimethylboranamine Me_2NBH_2 by a simple LCAO-MO Hückel treatment[760] is almost certainly very wide of the mark: because of π bonding the true value is likely to be well in excess of unity and nearer 2, since it is above the value of about 1·5 expected for borazines. Support for this conclusion is found in the circumstances that the energy barrier to rotation about the B—N bond in the unsubstituted boranamine H_2NBH_2 as calculated by the use of extended basis sets of Gaussian-type orbitals is 40·7 kcal mol^{-1} [761], compared with a mere 2·47 kcal mol^{-1} for ammonia borane $H_3N.BH_3$.[762] It would follow that the boron-nitrogen bond in boranamine has very marked double-bond character, and that with substituted boranamines $R^1R^2NBR^1R^3$ *cis* and *trans* isomers should exist, as has indeed been demonstrated by n.m.r. studies.[763]

The presence of donor and acceptor sites in the same molecule confers to the boranamines a more or less pronounced tendency to dimerize or oligomerize (p. 425). Such a change doubles the number of B—N bonds, but presumably weakens them and reduces the high force constants mentioned on p. 112. Thus, in the vapour phase, the N,N-dimethyl compound Me_2NBH_2 exists in equilibrium with its dimer, which has a $(BN)_2$ ring.[517, 523] In electronic terms this can be represented as:



However, steric and other factors play an important role, so that heats of dimerization vary widely (cf. Table XIV, p. 94). Thus many of the highly substituted boranamines exist only as monomers, whereas, as seen above (p. 92), the unsubstituted boranamine H_2NBH_2 preferentially exists as cyclic oligomers or polymers. But N-dimethylboranamine $HMeNBH_2$ appears to exist by preference as the cyclic trimer $(BH_2NHMe)_3$, and the reaction path by which the latter is formed has been clarified, at least in part.[764] In such a case there need be no disruption of the ring on further thermal decomposition to the borazine. This change will take place at a more moderate temperature when catalyzed by thiols[765]:



N,N′,N″-trimethylcyclotriboranamine 1,3,5-trimethylborazine

Unlike borazines, N,N′,N″-trimethylcyclotriboranamine $(BH_2NHMe)_3$ has a non-planar ring, and the existence of two conformational isomers has been demonstrated.[766] Even N,N-dimethylboranamine Me_2NBH_2 can be catalytically condensed to the trimer[767], although the condensed phase normally consists of the dimer: once formed, the trimer, whose molecular structure has been determined[768], shows exceptional thermal stability against dissociation. But in the case of N,N-dimethylboranamine there is also an important competing equilibrium in which dismutation to bis(dimethylamino)borane(3) $(Me_2N)_2BH$ occurs[523]

$$3Me_2NBH_2 \rightleftharpoons (Me_2N)_2BH + \mu\text{-}Me_2NB_2H_5$$

and this is therefore a further product which may be obtained from the interaction of diborane(6) and dimethylamine.

At rather higher temperatures in the range 100°–180°C, and preferably in sealed vessels, salts of polyhedral borane anions such as the icosahedral ion $B_{12}H_{12}^{2-}$ may be obtained from diborane(6) and either an amine or an amine borane[676, 769]:

$$2NR_3 + 6B_2H_6 \xrightarrow{100°\text{–}180°C} (NHR_3)_2[B_{12}H_{12}] + 11H_2$$

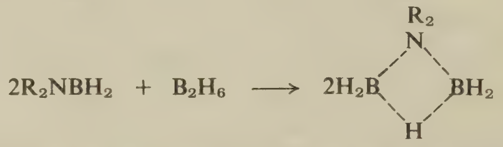
$$2NR_3.BH_3 + 5B_2H_6 \rightarrow (NHR_3)_2[B_{12}H_{12}] + 11H_2$$

The yield is very dependent on the nature of the amine. Under certain conditions the amine may in part finally appear in the anion, e.g. incorporated in the $B_{12}H_{11}NR_3^-$ ion, or in a non-ionic compound of the type $B_{12}H_{10}(NR_3)_2$. It may also appear in the cation as the ion $[H_2B(NR_3)_2]^+$ from asymmetric cleavage of the diborane(6). The complete picture of the possible reactions of diborane(6) with amines is thus still quite complex.

The reaction of B_2H_6 with ethylenediamine to give compounds which may or may not be cyclic is discussed on p. 87. With (dimethylamino)ethanol $Me_2NC_2H_4OH$, both addition and alcoholysis occur, and the final product is the borate ester $[Me_2N(BH_3)C_2H_4O]_3B$.[770]

With the cation $[Me_3PCH_2NMe_2]^+$ diborane(6) forms a simple ionic borane(3) adduct $[Me_3PCH_2NMe_2BH_3]^+$ [771], the first cation of this type to be discovered.

With amines substituted by inorganic groups, different types of reactions may occur with diborane(6). Compounds with boron already linked to the nitrogen are not excluded. Thus further diborane(6) will convert the above-mentioned boranamines into μ-aminodiboranes[518]:



With tetrakis(dimethylamino)diborane(4) $B_2(NMe_2)_4$, μ-$Me_2NB_2H_5$ may likewise be formed, but the adduct $B_2(NMe_2)_4.2BH_3$ is also produced, and this is thought to have a B_4H_{10}-like structure.[539] The product μ-$Me_2NB_2H_5$ undergoes isotope exchange with excess diborane(6).[733] In the presence of μ-$Me_2NB_2H_5$, diborane(6) will convert piperazine $C_4H_8(NH)_2$ at 100°C to piperazinobisdiborane(6) $C_4H_8(NB_2H_5)_2$.[772] With silylamines such as H_3SiNMe_2 and $(H_3Si)_2NMe$, diborane(6) gives the borane(3) adducts, at least initially, but these are decomposed irreversibly at 0°C[740]: no adduct is formed by trisilylamine $(H_3Si)_3N$.[543, 773]

With hydrazine N_2H_4, diborane(6) undergoes a reaction that may lead to ignition or explosion, but even here studies of the flame have shown[774–5] that there is initially a relatively low-temperature reaction which produces a hydrazine-diborane adduct; this changes by polymerization and dehydrogenation into largely uncharacterized solid products, including boron nitride.[776] In the high-temperature region radical mechanisms occur. At reduced temperatures the reaction can be made to proceed without ignition, and the original suggestion, based on the variable composition of the resulting mixture, was that the mono- and bis-borane adducts, $N_2H_4.BH_3$ and $H_3B.NH_2NH_2.BH_3$ (p. 24), are formed.[688] Both have since been isolated. Otherwise than with $N_2H_4.(BH_3)_2$, when the tetramethylhydrazine analogue $N_2Me_4.(BH_3)_2$ is heated, rupture of the N—N bond occurs. The products are hydrogen and a Me_2NBH_2-$B_2H_4(NMe_2)_2$ equilibrium mixture.[399] With acylhydrazines, the reaction of diborane(6) is normally reduction to the corresponding alkylhydrazines, but with 1,2-dibenzoylhydrazine considerable cleavage of the N—N bond has been observed.[613] With certain salts of hydrazine, such as its hydrochloride N_2H_5Cl in ether solution at room temperature, diborane(6) will give a polymeric material whose infra-red spectrum points to the $[N_2H_4.BH_2^+]_x$ grouping.[777]

Diborane(6) is liable to react explosively with hydroxylamine and certain of its derivatives, although borane(3) adducts can be obtained at low temperatures, as in the case of N,N-dimethylhydroxylamine.[778] Transferences of the oxygen to the boron also readily occurs, and in the case of O-methyl derivatives of hydroxylamine, the formation of the $>BOMe$ grouping has been observed[779]: however, these also give borane(3) adducts under appropriately controlled conditions.

Of the halogen-substituted amines, only dimethylchloramine Me_2NCl has been examined in respect of its reaction with diborane(6)[780], which is reported to be complicated. Although the reaction mechanism has not been elucidated, in the light of the reactions of this amine with other boron compounds it is probable that transference of the chlorine from the nitrogen to the boron is one of the changes that occur, expecially since dimethylamine is a product (cf. p. 20).

Almost no information is available concerning the behaviour towards diborane(6) of ionic species derived from ammonia or the ammonium ion, and this constitutes a considerable gap in our knowledge. However, it has been shown that the ionic species $Me_2NBH_3^-$ [525] and $Me_2N(BH_3)_2^-$ [781] are both converted to μ-dimethylaminodiborane:

$$Me_2NBH_3^- + B_2H_6 \rightarrow \mu\text{-}Me_2NB_2H_5 + BH_4^-$$

$$Me_2N(BH_3)_2^- + B_2H_6 \rightarrow \mu\text{-}Me_2NB_2H_5 + B_2H_7^-$$

Aromatic nitrogen also forms stable coordinate links with the BH_3 group, but the aromatic ring is not attacked by diborane(6). The first effect of B_2H_6 on pyridine is therefore normally to form the adduct $C_5H_5N.BH_3$, which is a substance of low volatility and m.p. 10°–11°C.[392] It is rather less stable with respect to dissociation than its trimethylamine analogue $Me_3N.BH_3$, so that the boron-nitrogen bonding is evidently less strong. A peculiar feature is that in diglyme solution excess B_2H_6 effects the formation not only of the diborane(6) adduct $C_5H_5N.B_2H_6$ at 0°C, but also of the triborane(9) adduct $C_5H_5N.B_3H_9$ at −64°C[387] (p. 178). The heats of reaction of diborane(6) with many substituted pyridines have been measured.[782–3] With ortho substitution, steric effects are very large. The n.m.r. spectra of the borane(3) adducts have been studied[784–5], and the merits of using the ^{11}B chemical shifts as a measure of donor-acceptor interaction discussed.[784]

Borazines are not usually attacked by diborane(6)[786], but aminoborazines react to give borane(3) adducts which decompose with cleavage of the exocyclic B—N bonds.[736]

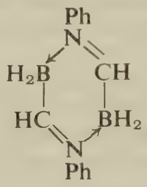
Pyridine N-oxide C_5H_5NO is reduced by diborane[786], but the ultimate products have not been identified.

Diazomethane reacts with diborane(6) at room temperature, but the reaction is unusual, in that the product is a highly linear methylene polymer.[787]

When the nitrogen is doubly bonded to carbon, the normal reaction with diborane(6) is reduction of the $>C{=}N\text{—}$ grouping to $>CH\text{—}NH\text{—}$, as in the case of oximes, oxime ethers, oxime esters and Schiff bases (p. 100), but additional reductions may also occur. With the ylide trimethylammonium methylide $Me_3\overset{+}{N}\text{—}\overset{-}{C}H_2$, neither adduct formation nor reduction appears to result with diborane(6) in tetrahydrofuran, and only a limited evolution of trimethylamine occurs[788]: this is in contrast to the reaction with ylides of phosphorus (p. 120) and sulphur (p. 131).

The cyano triple bond $\text{—}C{\equiv}N$ is readily reduced to the singly bonded $\text{—}CH_2NH_2$ grouping by diborane(6) in ether solvents.[442] In the absence of a donor solvent, however, the reaction proceeds differently, in that acetonitrile first gives the isolable adduct $MeCN.BH_3$, which has a rather weak boron-nitrogen bond and dissociates reversibly, and which on heating decomposes by hydrogen transfer to give a number of products, including 1,3,5-triethylborazine $B_3H_3N_3Et_3$ and μ-diethylaminodiborane(6) μ-$B_2H_5NEt_2$.[789–90] It is questionable whether the observed reactions with hydrogen cyanide and cyanogen $(CN)_2$ are comparable, as the products have not been characterized.[789] With inorganic cyanides a comparable reaction has not been observed: silyl cyanide H_3SiCN and its fully methylated derivative Me_3SiCN give the simple adducts $H_3SiCN.BH_3$ and $Me_3SiCN.BH_3$[608], and these on heating lose SiH_4 and $SiHMe_3$ respectively to leave polymeric BH_2CN as a glassy solid. Sodium cyanide NaCN however gives the ionic compound $Na[H_3BCNBH_3]$.[444] For other similar reactions with ions incorporating the cyano grouping, see p. 87.

Isocyanides react differently from cyanides. With diborane(6) at low temperatures phenylisocyanide gives, apparently, an adduct which is not isolated, but which immediately dimerizes with hydrogen migration to give a compound containing the 6-membered $(NCB)_2$ ring. Provided this is carried out in a non-polar solvent such as anhydrous petroleum ether, the first product isolated is I below, which still retains two hydridic hydrogen atoms per boron atom.[791] In dimethyl or diethyl ether as solvent,



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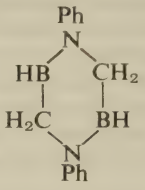

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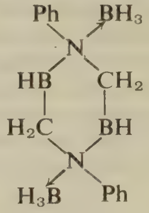


III

however, further migration of the hydrogen atoms from the boron to the carbon occurs and the product obtained, II, retains only one hydridic hydrogen atom per boron atom[729] and is capable of forming the bis-borane adduct III with additional diborane(6).

With metal cyanates in an ether, diborane gives borane(3) adducts.[443] With organic isocyanates, specifically with phenylisocyanate, reduction occurs[589], but the products have not been identified. Diborane(6) does not react chemically with silyl isocyanate, not even to form an adduct; however, it catalyzes the polymerization of the silyl isocyanate.[748]

With inorganic thiocyanates B_2H_6 gives a borane(3) adduct, but the infra-red spectrum accords better with a structure in which the BH_3 group is linked to the sulphur rather than the nitrogen atom.[444] There appear to be no reports of the behaviour of diborane(6) with organic thiocyanates or isothiocyanates.

It would be expected that diborane(6) reacts with most compounds containing multiple bonds between nitrogen atoms. There is, however no information published regarding its behaviour with the double bond in difluorodiazine N_2F_2, while the triple bond in N_2O is reported to be inert[793], as is that in the nitrogen molecule. With azobenzene, reduction accompanied by rupture of the N=N bond occurs[442], but not in the case of azoxybenzene.[589] With hydrogen azide in ether solution diborane(6) reacts at −20°C essentially according to the equation[794]

$$B_2H_6 + 6HN_3 \xrightarrow[-20°C]{Et_2O} 2B(N_3)_3 + 6H_2$$

but $BH(N_3)_2$ and $BH_2(N_3)$ are formed at the same time (see also p. 95). The reaction is completed at room temperature. With excess HN_3 an oil having the composition $HB(N_3)_4$ is obtained. With inorganic azides azidoborane $H_2B(N_3)$ is formed[445], but only in the case of the lithium salt has the simple borane(3) adduct $LiN_3.BH_3$ been shown to occur as an intermediate.

With compounds containing nitrogen linked to phosphorus, diborane forms adducts in which the boron is preferentially linked to the phosphorus (p. 32). An exception is the ylide $Ph_3\overset{+}{P}—\overset{-}{N}Ph$, which apparently gives the adduct $Ph_3PN(BH_3)Ph$.[409] No information is available regarding the behaviour of B_2H_6 with nitrogen linked to arsenic or antimony.

Knowledge regarding the reactions of B_2H_6 with nitrogen compounds containing oxygen is incomplete, but it has been shown that N_2O[793] does not react. Likewise NO is inert at room temperature, but general decomposition to hydrogen, N_2O and H_3BO_3 occurs at 90°C.[793] When subjected to an electric discharge, B_2H_6-NO mixtures give nitrogen and either hydrogen plus B_2O_3 or H_3BO_3.[795] The absence of lines from OH in the spectrum obtained from the reaction of diborane(6)-rich mixtures would indicate that the boron of the diborane(6) reacts with the nitric oxide so rapidly, that it is completely oxidized before the hydrogen can react. However, with other procedures there is evidence that the adduct $BH_3.NO$ can be formed as a transitory species.[793,796] No information is available for the behaviour of diborane(6) with the other oxides of nitrogen. With '$(NaNO)_x$'—actually *cis*-$Na_2N_2O_2$—the adduct $Na^+[ON.BH_3]^-$ is formed.[455]

With organic compounds containing nitrogen linked to oxygen, the general rule is that reduction occurs if the nitrogen is in the trivalent state, but not if it is in the pentavalent state. This suggests that reaction occurs by way of an addition complex, for the formation of which the presence of a lone electron pair on the nitrogen atom is required—an observation which also accords with the inertness of N_2O cited above. Thus nitroso compounds are attacked and converted to amines[628], while this is not true of nitro compounds.[589] It is even possible to conduct reactions involving B_2H_6 in nitrobenzene solution without interference from the solvent.[783, 797] This inertness towards diborane(6) is shared by azoxybenzene.[589] That nitronates[629] are however reduced, although the nitrogen is in its maximal valency state, implies that the mechanism here is different and presumably associated with the negative charge on the anion. Pyridine N-oxide constitutes another exception, since its nitrogen is reduced to the trivalent state.[589] With compounds containing the =N—OH or =N—OR grouping, such as oximes, oxime ethers and oxime esters[593], reaction occurs with the formation of amines by reduction via the corresponding N-substituted or, presumably, N,O-disubstituted hydroxylamines, which may be isolable; indeed, for certain oximes, e.g. that of benzophenone, the hydroxylamine constitutes the stage at which the reaction terminates. It thus follows that diborane(6) reacts reductively with some but not all nitrogen compounds containing the —NHOH group. The available evidence indicates that reaction with the —NHOR grouping occurs more readily, and that the product is invariably the amine.

Diborane(6) gives borane(3) adducts with compounds containing nitrogen linked to sulphur, but the boron is preferentially attached to the sulphur (cf. p. 37). Evidence is very limited, however, and not even the sulphide N_4S_4 has been investigated in this respect. There are no reports of studies with compounds containing nitrogen linked to selenium or tellurium.

Diborane(6) reacts with the gaseous trifluoride NF_3 on warming to give an uncharacterized yellow solid, but no new volatile products.[798] With tetrafluorohydrazine N_2F_4 at about 150°C a complex reaction occurs producing a mixture of BF_3, $H_3N.BF_3$, fluoroborazines, B_5H_9, H_2 and N_2.[799] Clearly the high affinity of boron for fluorine promotes hydrogen-fluorine exchange between the reactants. Presumably reaction would also occur with difluorodiazine N_2F_2, but this has not been put to experimental test. Compounds containing nitrogen linked to other halogens would also be expected to react with diborane(6), but only in the case of dimethylchloramine Me_2NCl[780] is experimental confirmation available, and even here the products have not been identified. The reaction is stated to be complicated.

REACTIONS WITH COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

The behaviour of diborane(6) with elementary phosphorus, arsenic, antimony or bismuth has not yet been reported. Although diborane(6) may on occasions be cleaved asymmetrically by compounds of trivalent phosphorus and arsenic, such cases are much rarer than with nitrogen compounds, and the products usually obtained are borane(3) adducts or, if hydrogen is lost, phosphino- and arsino-boranes. Information regarding the behaviour of diborane(6) with antimony compounds is scant, and totally lacking in the case of bismuth compounds.

The existence of phosphine adducts of undissociated diborane(6) has not been established, although numerous borane(3) adducts of phosphines, some of which are described on pp. 29 ff, have become known since phosphine borane $H_3P.BH_3$ (p. 28) was first reported in 1940[397] and later shown to be monomeric.[800, 398] However, its vapour is extensively dissociated at room temperature.[801] It is formed rather slowly from diborane(6) and phosphine at 0°C[801], at which temperature it is a solid with a saturation pressure of 200 Torr.[397] The kinetics of its formation are compatible with a symmetric cleavage of B_2H_6 by phosphine[801]; but it must be stated that they do not exclude the formation of a diborane(6) adduct, $H_3P.B_2H_6$, as the initial product, although no positive evidence for the existence of the latter has ever been found. The position is similar for the faster reactions between B_2H_6 and the methylphosphines.[802] The borane(3) adducts of substituted phosphines, which are described in detail on pp. 29 ff, may also be prepared by reacting the phosphine with B_2H_6 prepared *in situ* in a monoglyme solution from sodium tetrahydroborate(1–) and iodine.[757, 264]

One of the unexpected features of substituted phosphine adducts of type $RR'R''P.BH_3$ is their enhanced stabilities relative to those of the corresponding amine boranes. Thus the trimethylphosphine compound $Me_3P.BH_3$ is essentially undissociated in the vapour phase, even at 200°C.[803] The probable reason for this apparent anomaly is discussed on p. 27. It must be regarded as a function of the change undergone by the group-V atom on coordination, whereas the borane moiety shows little difference, whether linked to nitrogen or phosphorus: thus the B—H stretching frequencies in $Et_3P.BH_3$ are only very slightly lower than in $Et_3N.BH_3$.[804] The anomaly in the order of the dissociation energies of the coordinate bonds, namely $B \leftarrow P > B \leftarrow N$, is not reflected in the trend of the stretching force constants, which have been determined at 1·958 mdyne $Å^{-1}$ for the B—P bond in $H_3P.BH_3$[805] and 2·948 mdyne $Å^{-1}$ for the B—N bond in $H_3N.BH_3$.[806] In this connection, it should be mentioned that diborane(6) exhibits a progressively decreasing tendency to form stable borane(3) adducts with arsines and stibines, so that there is no anomaly here. Already in the case of arsenic, arsine borane $H_3As.BH_3$ is not isolable at atmospheric pressure, but as the arsine is progressively methylated, adducts of increasing stability, $H_2MeAs.BH_3$, $HMe_2As.BH_3$ and $Me_3As.BH_3$, are formed.[394]

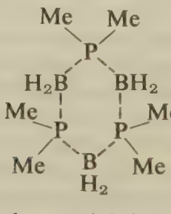
In confirmation of the above considerations, a further example of the importance of changes in the phosphine moiety on coordination is provided by the exceptional stability of difluorophosphine borane(3) $HF_2P.BH_3$ relative to $H_3P.BH_3$ and $F_3P.BH_3$[807], which has been ascribed to FHF interactions. And here it is to be noted that such interactions would be expected to increase and thus liberate energy as the phosphorus atom becomes coordinated, since this change would almost certainly be associated with a reduction in the non-bonded F···H distances.

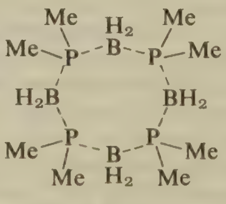
Other factors which affect the stability of the boron-phosphorus link in the substituted phosphine adducts include the base strength and especially the steric demands of the phosphine, as exemplified on p. 29. Phosphine boranes have been studied by means of their n.m.r. spectra[808–9], and also their magneto-optical properties, magnetic susceptibilities, and molecular refractions.[810–13] The temperatures of decomposition (as distinct from dissociation) have been studied for the borane(3) adducts of the trialkyl compounds of phosphorus, arsenic and antimony.[814]

Since phosphine boranes with hydrogen linked to the phosphorus, such as $HMe_2P.BH_3$, lose molecular hydrogen in the neighbourhood of 150°C to give polymeric phosphinoboranes[546] analogous to the boranamines (p. 112)

$$HR_2P.BH_3 \xrightarrow{\text{heat}} \frac{1}{n}(PR_2BH_2)_n + H_2$$

except that here n is usually 3 or 4 or a much higher number, it follows that the same products are produced direct from diborane(6) when it is allowed to interact with the phosphines at the appropriate elevated temperatures. When n is large, the product has the properties of a non-volatile polymer and is probably chainlike, but the trimer and tetramer are known to be cyclic[815–16]:



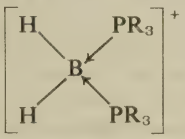


These compounds are rightly regarded as bridge-substituted derivatives of B_3H_9 (p. 181 and a hypothetical B_4H_{12} (p. 226) respectively. In neither case are the rings planar. Precisely comparable arsinoborane polymers are formed in a parallel manner, but at more moderate temperatures.[394] The exact nature of the P—B and As—B bonding is not known, but the P—B bond lengths are appreciably greater than those of the single

P—C bonds, i.e. respectively 1·935 and 2·08 Å as against 1·84 Å, suggesting an order of less than unity. Nevertheless, these compounds are surprisingly stable, both chemically and thermally: the B—H bonds have virtually lost their hydridic character and become very resistant to hydrolysis, even towards 4M HCl at 100°C[546], yet within experimental error retaining the same HBH bond angle[816] as in diborane(6); while in the absence of air the compounds will withstand prolonged heating to 250°C or more (200°C in the case of the arsenic compounds) without appreciable decomposition. The results of heating B_2H_6 with PH_3 and AsH_3 respectively are not cyclic compounds, but non-volatile solids, $(BPH_x)_n$ or $(BAsH_x)_n$, where $x<4$.[546, 394] The loss of more than 1 molecule of hydrogen from the simple adduct suggests a parallel with the B_2H_6-NH_3 system, which gives $(BNH_2)_n$ as well as $(BNH_4)_n$. Some observations[814] suggest that trisubstituted phosphine and arsine adducts of the types $R_3P.BH_3$ and $R_3As.BH_3$ can lose alkane RH on heating, which if established, is in contrast to the behaviour of tertiary amine boranes $R_3N.BH_3$, but finds a parallel in the loss of trimethylsilane $SiMe_3H$ by the trimethylsilyl compound $(Me_3Si)Et_2P.BH_3$ to leave $(Et_2PBH_2)_3$ on heating to temperatures > 80°C.[610] Moreover, the Si—P bond of Me_3SiPEt_2 is cleaved by B_2H_6. The same is true of $(Me_3Si)_3P$[743], in contrast to $(Me_3Si)_3N$[773], which does not react.

Phosphines with more electronegative substituents may also form borane(3) adducts with B_2H_6. Foremost among these is PF_3 which, in spite of its poor basic powers, gives $F_3P.BH_3$[268] (p. 34). The adduct, which is formed from diborane(6) and phosphorus trifluoride at room temperature under pressure, has a stability similar to that of borane carbonyl H_3BCO, which it also resembles in other ways. The much higher stability of $HF_2P.BH_3$[807] has already been commented upon (see also p. 35). The highly volatile but unstable complex $(CF_3)_2FP.BH_3$ can also be prepared[817] (p. 35). In adducts of the types $(RO)_3P.BH_3$ and $(R_2N)_3P.BH_3$, which are readily prepared from diborane(6) and trialkyl phosphites or tris(dialkylamino)phosphines respectively, the boron is always linked to the phosphorus rather than to the oxygen or nitrogen.[809–10, 812, 818–21] The same is true for the adducts formed with alkoxychlorophosphines, namely $Cl(RO)_2P.BH_3$ and $Cl_2(RO)P.BH_3$.[822] The boron is also attached to phosphorus in the BH_3 adducts of $Me(Et_2N)P(OCHMe_2)$[823] and $Me_2PCH_2NMe_2$[771], although the latter compound can also form a stable bis adduct, a power apparently not shared by bases in which the phosphorus and nitrogen atoms are directly linked. For adducts of compounds containing both phosphorus and sulphur, such as Me_2PCH_2SMe,[771] the boron links itself to the phosphorus rather than to the sulphur.

Other less simple reactions which diborane(6) may undergo with substituted phosphines and arsines at elevated temperatures to a large extent have their parallel in reactions with the amines. Thus cations of the type



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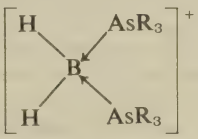


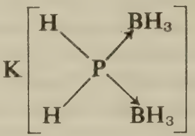
are readily formed.[769, 427, 676] At the same time some of the B_2H_6 condenses to form anions such as the dodecahydrododecaborate(2−) ion $B_{12}H_{12}^{2-}$ and its derivatives $B_{12}H_{11}(PR_3)^-$ or $B_{12}H_{11}(AsR_3)^-$, as well as the neutral species $B_{12}H_{10}(AsR_3)_2$. Compounds such as $[H_2B(PMe_3)_2]_2[B_{12}H_{12}]$ and $[H_2B(AsMe_3)_2][B_{12}H_{11}AsMe_3]$ have been proposed as pyrotechnics.[824].

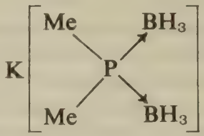
Both bisphosphines of the type HPhP—R—PHPh[825] and diphosphines such as P_2Me_4[400] and $P_2(NMe_2)_2$[401] form bis-borane(3) adducts (p. 32). Diphosphine adducts decompose on heating, e.g.[399]

$$Me_4P_2.2BH_3 \xrightarrow{220°} 2Me_2PBH_2 + H_2$$

when the phosphinoborane Me_2PBH_2 is obtained as a mixture of the trimer and tetramer.

If the hydrogen of a phosphine has been partly replaced by a metal, as in potassium phosphinide and dimethylphosphinide, KPH_2 and $KPMe_2$, a facile reaction with diborane(6) results in a bis-borane(3) ionic product in which the phosphorus in the anion is 4-coordinate[826]:





(see also pp. 29, 111). The complete replacement of phosphinic hydrogen by oxygen does not prevent the formation of several adducts by the P_4O_6 molecule[827] (see p. 34).

Because of their stability, there is in general little tendency for diborane(6) to react with compounds of pentavalent phosphorus. But the reduction of phosphine oxides[614–15] to phosphines constitutes an exception, and further exceptions are provided by the ylides such as $Ph_3P{=}CH_2$ or $Ph_3\overset{+}{P}{-}\overset{-}{C}H_2$, which give borane(3) adducts[408] (see p. 32). Arsenic-containing ylides such as $Me_3\overset{+}{As}{-}\overset{-}{C}HSiMe_3$[410] provide a parallel case.

Diborane(6) gives a blue coloration with phosphomolybdic acid, which has been proposed as the basis of a microanalytical method for the determination of diborane(6) and its derivatives.[731]

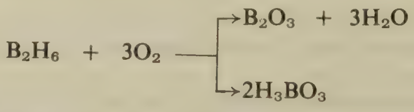
In spite of the relatively stable compounds formed by substituted arsines, no comparable products are formed at room temperature by substituted stibines and bismuthines, since reduction to the metal is effected by diborane(6), even in the case of the relatively stable triphenyl compounds Ph_3Sb and Ph_3Bi.[828] It has been reported that trimethylstibine gives a borane(3) adduct at low temperatures, but this decomposes at −35°C.[814]

REACTIONS WITH OXYGEN AND ITS COMPOUNDS

Diborane(6) burns in oxygen or air with the liberation of 517·6 kcal mol^{-1} on conversion to boric oxide and water, or 531·6 kcal mol^{-1} on conversion to boric acid, as calculated from heats of formation.[155] The heat of combustion, viewed in terms of heat per unit weight of fuel, is extraordinarily high and is exceeded only by the corresponding heats per unit weight for elemental hydrogen, beryllium hydride BeH_2 and beryllium tetrahydroborate $Be(BH_4)_2$. Consequently diborane(6) and its derivatives have in the past been much investigated as potential high-energy fuels and propellants; but to obtain the maximum energy the boric oxide formed needs to be in the condensed phase, and on account of this and other technical limitations and difficulties, neither diborane(6) nor any other boron compound has found any large-scale use for either purpose. In a welding torch diborane(6) can be made to give a flame temperature of over 3,000°C.

In contrast to higher boranes, pure B_2H_6 is stable towards oxygen at room temperature. The flash point for B_2H_6 of purity 99% in oxygen is stated to be 130°–135°C and in air 145°–150°C.[829] It is moreover not lowered by packing the reaction vessel with glass tubes. A slow reaction is however observable at temperatures as low as 110°C.[830] Kinetic studies of the diborane(6)-oxygen reaction above 120°C have been carried out.[831] No direct action is observed below 110°C, so that it is to be suspected that occasional reports of detonation of mixtures at room temperature after prolonged standing arise from other causes such as the accumulation of oxgyen-sensitive products from a slow spontaneous decomposition of the B_2H_6. This explanation is the more likely because the presence of hydrogen both inhibits these explosions[829] and inhibits the decomposition of B_2H_6.[161, 18]

The reaction with oxygen in both explosion and combustion has been much studied. Of the two conceivable reactions with excess oxygen, *viz.*



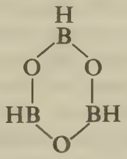
$$B_2H_6 + 3O_2 \longrightarrow \begin{cases} B_2O_3 + 3H_2O \\ 2H_3BO_3 \end{cases}$$

the former is favoured by the bulk of the evidence.

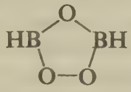
Mixtures of diborane(6) and oxygen containing between 2·0 and 27·6% of the former can be detonated on sparking.[832] Detonation velocities up to 2·6 km s^{-1} have been observed[833], a very high value. In early work on the explosion reaction, first, second and third explosion limits were recognized[829], the third limit being found sensitive to the diameter of the reaction vessel. The inhibiting effects of gaseous hydrogen, nitrogen and excess oxygen respectively were also reported. The effect of many other inhibitors has since been studied: butadiene and toluene were found to be very effective[834], as is iron pentacarbonyl.[835] Small proportions of nitrogen dioxide (1·2%) actually reduce the explosion temperature to as low as 74°C, but larger amounts increase it again.[836] Nitric oxide effects immediate explosion at room temperature. On the other hand, under non-explosive conditions in the neighbourhood of 150°C, diborane(6) actually decomposes more slowly in the presence of added oxygen than in its absence. The reaction mechanism of the B_2H_6-O_2 reaction is imperfectly understood, but it is generally agreed to be typical of a branching-chain free-radical mechanism. The evidence with additives implies that the chain-branching step is bimolecular and the chain-breaking step termolecular. The radical involved in the chain-branching–chain-breaking competition may, according to different proposals, be BH_3O_2[831] or $B_3H_7O_2$[834]; indeed, the presence of both species as intermediates had been proposed earlier.[837] The species BH_3O_2 has a parallel in compounds of the type $R_3B.O_2$ observed to be the initial products in the reaction of oxygen with trialkylboranes.[838] If $B_3H_7O_2$ predominates in the above-mentioned competition, then the suggested mode of formation[834] is less likely than the step

$$B_3H_9 + O_2 \rightarrow B_3H_7O_2 + H_2$$

since the slow oxidation reaction is of order 1·5 with respect to the diborane(6) concentration[837], while the floating concentration of the triborane species B_3H_9 is also proportional to $[B_2H_6]^{1\cdot5}$.[18] This, surely, is more than coincidence. The low value of $[B_3H_9]$ would also explain why the rate is independent of the oxygen concentration for measurable values.[837] Of the incompletely oxidized boron products, one which has been definitely identified by mass spectroscopy in the explosion reaction is the cyclic compound boroxine $H_3B_3O_3$[839], which has the structure



Both in the explosion reaction[837] and in mixtures subjected to an electric discharge[380] the additional species $H_2B_2O_3$ has been demonstrated to be present. This has been ascribed the structure



Both species occur in the photochemical oxidation of diborane(6) by oxygen[840], in which $H_2B_2O_3$ arises from a slow initial reaction and $H_3B_3O_3$ from an explosive reaction. A proposed intermediate in their formation is B_2H_4O, but positive evidence for this is lacking. In fuel-rich explosions, molecular hydrogen is a major product and may account for virtually all the hydrogen present, except that in very rich mixtures a significant proportion may remain in the solid reaction products.[841] The appearance of molecular hydrogen rather than water is indicative of the much higher affinity for oxygen displayed by the boron. This is also likely to be the explanation for the fact that hydroxl radicals have not been detected spectroscopically in chemical detonations, although they appear in the flash-photolyzed reaction.[358] Other studies of the explosion reaction include the variation of the detonation rate[832], which is predictable from thermodynamic data for mixtures containing up to 12% of B_2H_6, but becomes unpredictably high for richer mixtures, possibly on account of condensation of products just beyond the wave front.

Diborane(6) flames have also received study. Early work showed that diborane(6)-oxygen mixtures containing 0·9–98% of B_2H_6 will support a flame, so that the flammability limits are exceedingly wide.[833] The corresponding range for diborane(6)-air mixtures is 0·8–87·5% by volume, according to one particularly valuable study.[842] However, the non-detonating region of flammability on the fuel-lean side is seen to be narrow, being restricted to the range 0·9–2·0% of B_2H_6. Flame speeds are exceedingly high, the highest so far measured, the quenching diameter falling to a small fraction of 1 mm.[843] In the early work speeds of 100 $m\ s^{-1}$ were reported[833], namely 20–100 times those of hydrocarbon flames, but these may refer to mixtures just inside the detonating region, since detonations sometimes occurred after the flame had travelled a limited distance. For diborane(6)-air mixtures at 25°C, the maximum burning velocity observed is about 5 $m\ s^{-1}$ [842], more than a power of 10 above the rate for propane-air mixtures. Although small quantities inhibit slightly[844], the addition of about 6% of B_2H_6 to propane or isobutane effects a marked increase in the burning velocity of the gas.[845] For larger additions, a selective burning of the diborane(6) becomes apparent. With propane containing 15% of admixed B_2H_6, burning velocities show two maxima, one where the proportion of air is close to stoichiometric for the B_2H_6 alone, and one where it is about stoichiometric for the total fuel.[842] At the first maximum the propane is behaving mainly as a diluent reducing the temperature of the flame, although it undergoes some cracking. But as the proportion of oxygen rises, increasing oxidation of the propane is accompanied by a reduction in the flame velocity until the minimum between the two maxima is reached. This may be regarded as *prima facie* evidence that at least one oxidation product of the hydrocarbon is acting as an inhibitor of the B_2H_6-O_2 reaction. Such mixtures do not follow the Spalding rule[846] concerning flame speeds for mixtures. That the diborane(6) is burnt before much oxygen is consumed by the hydrocarbon, is doubtless a reflection of the higher affinity for oxygen possessed by boron relative to that possessed by carbon, and is also manifest in the structure of flames of B_2H_6-C_3H_8 mixtures.[842] These manifest three zones, a lower sky-blue luminous cone or region of diborane(6) oxidation emitting the α bands of BO superposed by an intermediate non-luminous zone, above which is situated the luminous hydrocarbon-combustion mantle. The latter emits the green so-called 'fluctuation' bands of boric oxide. Even though some cracking and partial oxidation of the hydrocarbon must occur in the first zone, it is clear from this that the organic species present burn much more slowly than the diborane(6). Similar distinct zones are apparent when B_2H_6 is burnt without added hydrocarbon, save that with flames near the fuel-lean limit the temperature of the final zone may not be hot enough to effect the emission of the green fluctuation bands. In these flames the boron is burning before the hydrogen:

$$B_2H_6 + 1\tfrac{1}{2}O_2 \rightarrow B_2O_3 + 3H_2$$

Further, experimental evidence of a variety of kinds indicates that the combustion of the boron is virtually complete before any water is formed. Indeed, with flames near their B_2H_6-lean limit, even in spite of the large excess of oxygen, a considerable proportion of molecular hydrogen is present just downstream of the luminous reaction zone and is only oxidized subsequently.[842] It follows that there is no evidence for the formation of any water at a point early enough to hydrolyze unburnt B_2H_6.

The sum of the evidence is still to leave even the nature of the products of diborane(6) flames inadequately known, especially on the diborane-rich side. Consequently no convincing oxidation mechanism covering the reaction within the flame has been advanced. In a most useful review of the available knowledge[750], possible mechanistic pathways have been tentatively suggested. The gaseous products present in the flame include the species BH, B, BO, B_2O_2, B_2O_3, BO_2, HBO_2, H_3BO_3, H_2, OH and H_2O, of which only OH has not been positively observed. Some of these may also be present as condensed species. There is reason to believe that the following additional gaseous species are probably present in the flame: BH_3, B_3H_9, BH_3O_2, $B_3H_7O_2$, BHO and $(BHO)_3$. For these, confirmation is at present lacking. Despite this array, yet other species are not excluded. The reaction system is therefore much more complex than the hydrocarbon-oxygen reaction system. The intrusion of the formerly unsuspected species $BO_2(g)$ is to a considerable degree responsible for reducing the temperature of the flame[750] and hence the impulse achievable from diborane(6) and other borane fuels, though this is not the only reason that these fuels have fallen below the expected performance.

The light emitted in the chemiluminescent reaction between diborane(6) and both molecular and atomic oxygen has been studied.[847] The products of the reaction with atomic oxygen have also been investigated.[848] This reaction occurs at room temperature and probably well below. The photochemical decomposition of nitrous oxide was used as a source of oxygen atoms. The initial products are confined to the molecular species H_2, B_4H_{10}, B_5H_9 and a white solid of formula $(BHO)_n$. The initial step is apparently

$$B_2H_6 + O \rightarrow BH_3O + BH_3$$

but there is a faster reaction

$$B_4H_{10} + O \rightarrow BH_3O + B_3H_7$$

which competes for the oxygen atoms and keeps down the concentration of B_4H_{10}.

There is no information regarding the reaction of diborane(6) with ozone.

Turning now to reactions with oxygen compounds, the first observation which must be made is that, notwithstanding the two lone pairs of electrons normally present on the oxygen atom, the formation of stable borane(3) adducts by diborane(6) does not dominate the overall picture here as it does with nitrogen and phosphorus compounds, or even to some extent with sulphur compounds. There are two main reasons for this. First, in most cases other more extensive reactions usually occur, even at room temperature. Secondly, even with compounds which undergo such reactions either not at all or only slowly, e.g. ethers, the donor powers towards borane(3) of the oxygen are so far depressed relative to those of nitrogen, that the borane(3) adducts are too unstable to be isolated at room temperature, although frequently they can be shown to be present in solution. Nevertheless, if the borane(3) is already part of an adduct, as in $Me_3N.BH_3$, $C_5H_5N.BH_3$ or $Et_3P.BH_3$, there is spectroscopic evidence that hydroxy compounds such as alcohols and phenols will form hydrogen bonds with the borane(3) moiety, the boron acting as proton acceptor.[849]

In its reaction with water, diborane(6) is very rapidly hydrolyzed completely in a highly exothermic reaction, the heat of which has been accurately measured as $111{\cdot}46 \pm 0{\cdot}54$ kcal mol^{-1}.[153] A six-fold volume of hydrogen is liberated according to the equation

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

and until comparatively recently all attempts to identify any intermediates in the reaction proved fruitless. The initial step is probably the formation of an adduct, and $H_3B.OH_2$ was proposed.[850] The existence of this transitory species is also strongly implied by the kinetics of the low-temperature hydrolysis of the BH_4^- ion.[851] But definite evidence is now claimed for the existence at −130°C of $B_2H_6.2H_2O$[852], which might be suspected to be of the form $[BH_2(OH_2)_2]^+[BH_4]^-$, although it could be $H_3B.OH_2$. It is difficult to avoid the assumption that in the hydrolysis of diborane(6) the hydrogen is liberated through successive replacement of hydrogen atoms by hydroxyl groups: yet no partially hydroxylated derivatives have been isolated in the reaction of a small amount of water with a large excess of diborane(6)[850], where the products are only boric acid and hydrogen with unchanged B_2H_6. It follows that any partially hydroxylated derivatives formed must disproportionate very rapidly into boric acid and diborane. Nevertheless, hydrolysis of diborane(6) with ice at −80°C does not proceed to completion, but yields only four molecules of hydrogen per molecule of B_2H_6. The B_2H_6-H_2O reaction is first order with respect to $[H_2O]$ and 0·5 order with respect to $[B_2H_6]$.[850]

Under strongly acid conditions, e.g. 8M HCl, hydrolysis yields only two molecules of hydrogen at −75°C, the remaining four molecules being liberated on warming to above −20°C.[853–4] This has been interpreted in terms of the formation and subsequent decomposition of aquated BH_2^+, which in the light of further knowledge, is in all probability the ionic species $[BH_2(OH_2)_2]^+$. Under strongly alkaline conditions hydrolysis yields only a limited amount of hydrogen, and the principal product is a tetrahydroborate together with some metaborate.[730, 854] A combination of the following equations may explain the products:

$$2B_2H_6 + 4OH^- \rightarrow 3BH_4^- + B(OH)_4^-$$
$$B_2H_6 + 2OH^- + 2H_2O \rightarrow BH_4^- + B(OH)_4^- + 2H_2$$

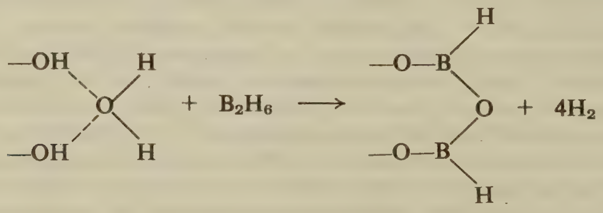
The ion $BH(OH)_3^-$ has been considered as another product of this reaction, but attempts to detect it from the ^{11}B n.m.r. spectrum failed.[854] However, there is evidence of its presence during the alkaline hydrolysis of the BH_4^- ion.[851] The reaction of B_2H_6 with alkaline D_2O has also been studied.[855] The hydrogen liberated is mostly $^1H_2$ and is not significantly contaminated with the mixed isotopic species HD. Of the two possible mechanisms, the results favour that involving asymmetric cleavage through coordination, as originally suggested.[856]

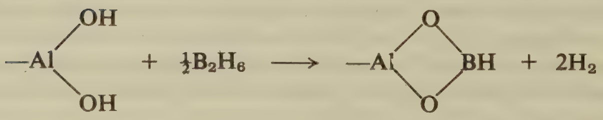
After earlier studies with 'bound water' of silica gel[857] and silica-alumina catalysts[858], the reaction of diborane(6) with the water of constitution of various hydrated inorganic solids was studied on a quantitative basis.[859] For every molecule of B_2H_6 consumed, the water of crystallization was considered to liberate two molecules of hydrogen, but hydroxl groups only one, whereas complete hydrolysis would have liberated six. This is explained for the example of silica gel by the changes:

$$\geqslant Si{-}OH\cdots OH_2 + B_2H_6 \longrightarrow \geqslant Si{-}OH\cdots O(BH_2)_2 + 2H_2$$

$$\geqslant Si{-}OH + B_2H_6 \longrightarrow \geqslant Si{-}OB_2H_5 + H_2$$

The concentration of —OH groups on the surface has been measured by means of the observed hydrolysis.[860] It has, moreover been claimed that the spectroscopic properties of the surface in the infra-red region differ according to whether BH_2 or BH_3 groups are on the surface.[861] Later workers have however concluded that the above reaction does not permit the making of a distinction between water molecules and silanol groups in silica gel.[862] Still later, other investigators found that frequently more than two molecules of hydrogen are liberated for every molecule of diborane(6) consumed, and concluded that the figure was >2 for hydration water and $\leqslant 2$ for silanol groups.[863–4] According to this view, terminal $—B_2H_5$ groups are not formed, only $>O{:}BH_3$, $—BH_2$ and $>BH$ terminal groups, the latter arising from hydration water or from adjacent hydroxl groups:





From what is known of the chemistry of diborane(6), it must be admitted that the formation of $—OB_2H_5$ groups is rather unlikely; and it is still more difficult to accept the more recent suggestion that the surface of γ-alumina contains O^{2-} ions which coordinate weakly with diborane to produce linear polyboranes.[865] But it cannot be claimed that the differences between the various opinions have been finally resolved. However, three different $>$BH surface structures prepared by another method have now been spectroscopically recognized.[866] Certainly treatment with diborane(6) enhances the catalytic activity of surfaces of silica-aluminas through partial hydrolysis of the B_2H_6, and the practical details of a useful procedure have been published.[867]

With alcohols, adducts of formula $B_2H_6.2ROH$ are formed at low temperatures[852], in analogy with the behaviour of B_2H_6 with water. Diborane(6) undergoes alcoholysis at ordinary temperatures, but the release of hydrogen is much less violent than in hydrolysis. By comparison with water, the reaction may be rather sluggish, especially in the later stages. With methanol, for example, the ultimate product is trimethyl borate, but otherwise than in the reaction with water a rather stable intermediate, dimethoxyborane $BH(OMe)_2$, can be isolated[272]:

$$4MeOH + B_2H_6 \rightarrow 2BH(OMe)_2 + 4H_2$$

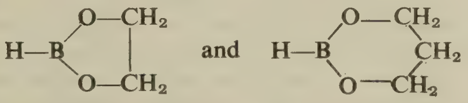
$$2MeOH + 2BH(OMe)_2 \xrightarrow{\text{slow}} 2B(OMe)_3 + 2H_2$$

A total of six molecules of hydrogen is liberated, and the second stage is observed to be much slower than the first. A white solid by-product is observed, which is possibly polymeric methoxyborane $(BH_2OMe)_x$, since it disproportionates into diborane(6) and $BH(OMe)_2$ or $B(OMe)_3$. The intermediate $BH(OMe)_2$ has a boiling point of 26°C, and even in the absence of excess methanol is slowly converted to $B(OMe)_3$ by disproportionation:

$$6BH(OMe)_2 \rightleftharpoons 4B(OMe)_3 + B_2H_6$$

Its infra-red spectrum is known[868], as are those of other dialkoxyboranes.[869–70] A study of the ethanolysis of B_2H_6 and B_2D_6 with ordinary and labelled ethanol has been described.[871] In the presence of a third substance such as iodine, aliphatic alcohols undergo a much more rapid low-temperature reaction with diborane(6).[430] This reaction is comparable with that undergone by aliphatic ethers in like circumstances, and to avoid repetition these reactions are discussed together on p. 127.

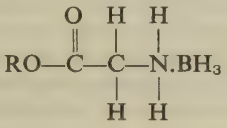
Alcoholysis of diborane(6) by the dihydric alcohols $HO(CH_2)_nOH$, where $n = 2$ and 3, respectively, leads to the cyclic compounds[872–3]



These disproportionate reversibly into diborane and bicyclic compounds of the type $\overline{O(CH_2)_nOB}\overline{O(CH_2)_nOB}O(CH_2)_nO$.

The alcoholysis of diborane(6) can be used as a means of determining the hydroxyl groups present in organic compounds.[874–5] This method depends upon the fact that only $-\!\!>$C—OH and not simple alkoxy or other $-\!\!>$C—OR groups are attacked at ordinary temperatures.

Accordingly ethers would be expected to be stable in contact with diborane(6), and, within the limitations mentioned below, this is borne out by observation. This provides opportunity for adduct formation, but in spite of the high solubility of diborane(6) in ethers no adducts are stable at room temperature. Accordingly it must be concluded that coordinate bonds from oxygen to borane(3) or diborane(6) are very much weaker than those from nitrogen. This is in harmony with the observation that simple borane(3) adducts with aminoacid esters contain the borane linked to the nitrogen atom and not to the oxygen atom of the carbonyl or alkoxyl group[876]:



$$RO\text{—}\overset{O}{\overset{\|}{C}}\text{—}\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{—}\underset{H}{\underset{|}{\overset{H}{\overset{|}{N}}}}.BH_3$$

However, evidence for loose adduct formation with simple ethers at low temperatures is well documented. Thus the n.m.r. evidence from ether solutions of diborane(6) is quite convincing in the case of dimethyl ether and tetrahydrofuran[877], and only slightly less so in the case of diethyl ether[877, 138], where even at temperatures as low as −80°C the adduct is apparently still undergoing fast equilibration. In the latter case it has been claimed that the very transient adduct is $Et_2O.B_2H_6$[138], and there is independent kinetic confirmation that this is indeed first formed[584], although the adduct is assumed by many workers to be $Et_2O.BH_3$. At all events, the latter also appears to have existence, since the internal chemical shift of the alkyl protons of the complex is observed to be the same within the limits of measurement as for the complex $Et_2O.BMe_3$.[878] Phase studies suggest two very weak complexes of formulae $Et_2O.BH_3$ and $Et_2O.B_3H_9$[879], but the variation in melting point over a very wide range of concentration is sufficiently small to leave room for doubt. Methyl ethyl ether provides definite evidence for a single complex of formula $MeEtO.B_2H_6$.[879]

Dimethyl ether, on the other hand, is a somewhat stronger base and definitely forms the adduct $Me_2O.BH_3$, since this can be isolated as a solid at −80°C[396, 879], albeit with an appreciable dissociation pressure. The still more basic tetrahydrofuran gives the adduct $(CH_2)_4O.BH_3$, which can be isolated below its melting point of −34°C.[880, 879] These adducts are probably not formed in one step, since in the case of tetrahydrofuran there is kinetic evidence implying that $(CH_2)_4O.B_2H_6$ first occurs.[584] Both adducts are completely dissociated in the vapour phase.[396, 881] The fully fluorinated ethers $(C_2F_5)_2O$ and cyclo-C_4F_8O form no adducts with diborane(6).[879]

In the liquid phase some ethers show signs of reacting in other ways than undergoing simple adduct formation, since diborane(6) dissolved in them confers on the solution with some powers of conducting an electric current.[431] Provided this is not due to contaminants such as BF_3, which might be present as an impurity in the diborane(6), this would seem to imply the existence of an ionization equilibrium, e.g.

$$2R_2O + B_2H_6 \rightleftharpoons [BH_2(OR_2)_2]^+ + BH_4^-$$

The matter merits further investigation and is in need of complete clarification.

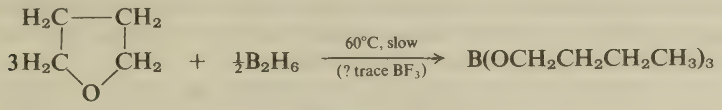
As mentioned on p. 123, the reaction between diborane(6) and water is so complete, that no hydroxy derivatives of B_2H_6 or BH_3 other than orthoboric acid $B(OH)_3$ can be isolated from this reaction. The result of interacting a little water with excess diborane(6) is always orthoboric acid, hydrogen and unchanged B_2H_6. The feasible intermediates B_2H_5OH, BH_2OH and $BH(OH)_2$ have never been prepared. However, it is hard to see how boric acid can be formed without the transitory existence of H_2BOH and $BH(OH)_2$, and mass-spectral evidence for their existence in the presence of B_2H_6 and $B(OH)_3$ when the latter are allowed to stand in contact has been forthcoming.[882] It has even been possible to estimate the enthalpies of formation of the vapours of both of the hydroxyborane(3) species from their equilibrium concentrations.[882] Their non-isolation must therefore be attributed to thermodynamic instability coupled with extreme kinetic instability. The alkoxy compounds H_2BOR and $HB(OR)_2$ are likewise thermodynamically unstable with respect to B_2H_6 and the trialkylborate $B(OR)_3$, and members of the H_2BOR series are also kinetically unstable and cannot be isolated, but can apparently be stabilized by coordination, e.g. with ether.[430] Dialkoxyboranes, on the other hand are isolable, as was first shown for $HB(OMe)_2$ by controlled alcoholysis of B_2H_6[272], but they readily disproportionate:

$$B_2H_6 + 4MeOH \rightarrow 2HB(OMe)_2 + 4H_2$$

$$6HB(OMe)_2 \rightleftharpoons B_2H_6 + 4B(OMe)_3$$

Lehmann and co-workers have reported the infra-red spectra of $HB(OMe)_2$[868], $HB(OEt)_2$[869] and $HB(OCHMe_2)_2$.[870] Particular interest is attached to the vibrational frequencies of the B—O bonds, which have been studied for a number of related molecules.[883] Some strengthening of the bond by π bonding might be expected, and rather persuasive evidence for this is found in the low-temperature n.m.r. spectra of Me_2BOMe and $(Me_2B)_2O$; the energy barriers to free rotation about the B—O bonds in both compounds are found to amount to *c.* 8·5 kcal mol^{-1} [556], a value about three times that found for the energy barriers to free rotation about the C—O bonds in methyl ethers.

In accordance with the high affinity of boron for oxygen, diborane(6) will slowly cleave some ethers to produce alkoxyboranes and ultimately trialkyl borates. Thus with excess tetrahydrofuran at 60°C, the diborane(6) is completely converted within 64 h to tri-*n*-butyl borate[601], while with diglyme a similar reaction occurs in which methyl groups are displaced as methane[604, 195]:



$$3(MeOC_2H_4)_2O + \tfrac{1}{2}B_2H_6 \xrightarrow[\text{(? trace BF}_3)]{\text{slow}} B(OC_2H_4OC_2H_4OMe)_3 + 3CH_4$$

That a borate ester is also formed in the last reaction, is confirmed by the formation of diethylene glycol monomethyl ether $HOC_2H_4OC_2H_4OMe$ on subsequent treatment with alkaline hydrogen peroxide. But it must be emphasized that it cannot be regarded as certain that the above ether-cleavage reactions occur with BF_3-free B_2H_6 (cf. p. 99), since BF_3 is known to catalyze the cleavage of ethers by diborane(6), and will further effect the cleavage of benzyl-oxygen bonds in a reaction[884] which clearly[235] produces diborane(6) *in situ*. Indeed, it has been tentatively concluded that the instability of solutions of diborane(6) in ethers is due to the presence of traces of BF_3.[222] This conclusion seems all the more likely because a sample of diborane(6) stated to be pure was observed to react with diisopropyl ether at elevated temperatures in quite a different sense, liberating not propane but hydrogen[603]:

$$3(i\text{-Pr})_2O + B_2H_6 \xrightarrow[6h]{80°C} PrB(O\text{—}i\text{-Pr})_2 + Pr_2BO\text{—}i\text{-Pr} + 3H_2$$

Propylboroxine is a by-product. Certainly it has been observed that boron trifluoride catalyzes the ring cleavage of epoxides[600], but epoxide rings are apparently also cleaved without a catalyst.[579, 597, 589] The mechanism has been studied.[598]

In the presence of a third substance, diborane(6) will sometimes cleave aliphatic ethers and alicyclic ethers in a most remarkable low-temperature reaction.[885] It undergoes a similar reaction with aliphatic alcohols. Thus in the presence of iodine[886] or bromine[887] (chlorine is inconveniently reactive) and with excess of the respective ether or alcohol, the oxygen atom of the cleaved C—O bond attaches itself to boron, while the carbon atom becomes linked to halogen:

$$B_2H_6 + 6R_2O + 3I_2 \rightarrow 2B(OR)_3 + 6RI + 3H_2$$

$$B_2H_6 + 6ROH + 3I_2 \rightarrow 2H_3BO_3 + 6RI + 3H_2$$

$$B_2H_6 + 6(CH_2)_nO + 3I_2 \rightarrow 2B(O(CH_2)_nI)_3 + 3H_2$$

No solvent is required. This is a highly efficient way[888] of converting alkyl ethers or aliphatic alcohols to alkyl iodides, and cyclic ethers to ω-iodoalcohols, which are formed on subsequent hydrolysis of the boric ester first produced. No iodine is lost, but when bromine is used some hydrogen bromide is formed in a side reaction, presumably by direct action with the diborane(6). The main reaction proceeds via intermediates such as the iodoborane adduct $R_2O.BH_2I$, as is clear from a study of the kinetics of the reaction in the inert solvent cyclohexane at low temperatures[430, 889]; but these intermediates are not generally isolable, except that in the case of diethyl ether the ionic substance $[BH_2(OEt)_2]^+I^-$ has been observed to be thrown out of solution and subsequently redissolve as it reacts further. Although the nature of the dealkoxyhalogenation reaction at the carbon atom of the cleaved C—O bond has not been definitely established, it is probably S_N2 since the comparable dehydroxyhalogenation reaction at the asymmetric carbon atom of an optically active alcohol proceeds with inversion of configuration.[890] On the other hand, in a similar dealkylation reaction involving

$NaBH_4$ in place of B_2H_6 retention of configuration has been reported.[891] In the above dealkoxyhalogenation reaction an alkyl group is transferred from oxygen to halogen. Other oxygen-containing organic compounds undergo comparable reactions, including epoxides, aldehydes and ketones[888], though in the case of epoxides hydrolysis of the boric ester initially formed is required to obtain an organic halide, while with the carbonyl compounds additional reduction by the diborane(6) occurs; and with organic esters[892] the reaction is associated with both additional reduction and the need to hydrolyze the first product. Ethers also undergo a rather similar reaction in which the third substance is a mercaptan instead of free halogen, when the diborane(6) effects the transfer of an alkyl group from oxygen to sulphur with the formation of a sulphide in good yield.[893] By analogy, the expected reaction is

$$B_2H_6 + 6R_2O + 6R'SH \rightarrow 2B(OR)_3 + 6RSR' + 3H_2$$

Diborane(6) is thus a reagent of much promise in alkyl-transfer reactions.

The action of diborane(6) on almost all other oxygen-containing organic compounds such as aldehydes, ketones, carboxylic acids and esters, lactones, acetals, ketals, *p*-benzoquinone and amides is to reduce them as noted in connection with its reducing properties on p. 100. Little is known about the precise mechanisms of these reactions, except in the case of that with acetone

$$4Me_2CO + B_2H_6 \rightarrow 2(Me_2CHO)_2BH$$

where the kinetics are first-order with respect to the concentrations of both reactants.[584] Alkoxyl and aroxyl groups are not affected by diborane(6), but oxygen bound in other ways, as in the carbonyl group, is normally reduced to hydroxyl, though subsequent hydrolysis of an intermediate boron ester may be required: only by exception does reduction proceed further and lead to replacement of the hydroxyl group by hydrogen, as when a coordinating substance (i.e. acceptor such as BF_3) is present as catalyst, or when strongly electron-withdrawing systems are attached to the carbon atom, e.g. in substituted perhydropyridazine-3,6-diones.[613]

Reduction also frequently occurs with compounds in which the oxygen is directly attached to an element other than carbon, as with alcoholates of alkali[720, 218] and alkaline-earth[721] metals, which are converted to tetrahydroborates, as noted on p. 109. Boron compounds such as dialkoxyalkylboranes $R'B(OR)_2$[480] and alkoxydiphenylboranes Ph_2BOR[481] are also reduced, although here the substitution of the —OR group by a hydrogen atom is reversible and accompanied by disproportionation. With aluminium triisopropoxide, partial reduction occurs with the formation of a complex of formula $Al(BH_4)_3.3Al(O\text{—}i\text{-}Pr)_3$, which can be distilled unchanged at low pressures[302]:

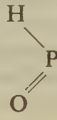
$$4Al(OPr^i)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3.3Al(OPr^i)_3 + B(OPr^i)_3$$

In all these reactions the boron becomes attached to the oxygen with the displacement of another element, which also occurs with oxygen compounds of silicon, tin and lead, as exemplified by disilyl ether[609], diethyldimethoxytin[610] and triethylmethoxylead.[723] In these cases the product is a hydride or sometimes a tetrahydroborate, as, surprisingly, in the case of the lead compound:

$$4(H_3Si)_2O + B_2H_6 \rightarrow 4SiH_4 + 2BH(OSiH_3)_2$$

$$2Et_2Sn(OMe)_2 + B_2H_6 \rightarrow 2Et_2SnH_2 + 2BH(OMe)_2$$

$$4Et_3PbOMe + 3B_2H_6 \rightarrow 4Et_3PbBH_4 + 2BH(OMe)_2$$

If the oxygen is linked to nitrogen, diborane(6) usually effects reduction, the oxygen being removed to leave an amine or a substituted hydroxylamine, a reaction discussed in more detail on p. 116. That nitrous oxide[793], azoxybenzene[589] and nitrobenzenes[589] do not react under ordinary conditions is most likely explained by high activation energies, that is, to kinetic rather than thermodynamic factors. When oxygen is singly linked to phosphorus, as in dialkyl phosphonates  $\overset{\mathrm{H}}{\underset{\mathrm{O}}{\mathrm{P}}}(\mathrm{OR})_2$[894] and trialkylphosphites

P(OR)$_3$[820], no reduction occurs with diborane(6) at ordinary temperatures, but with trialkylphosphites there is evidence that reduction sets in at elevated temperatures to form compounds of type (RO)$_2$PBH$_2$. Phosphine oxides R$_3$P=O lose their oxygen and yield phosphines.[614–15] Phosphoric acid and its derivatives are resistant to such reduction, and it is possible to prepare diborane(6) in the presence of anhydrous phosphoric[252] or fluorophosphoric acid.[256] Information is lacking concerning the behaviour of B$_2$H$_6$ with oxygen compounds in which the oxygen is linked to arsenic, antimony or bismuth.

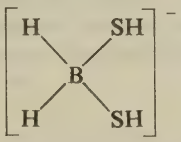
There are very few published data concerning the behaviour of B$_2$H$_6$ with compounds containing oxygen linked to sulphur, and none at all about that with compounds in which oxygen is linked to selenium or tellerium. Diborane(6) is destroyed by sulphur dioxide in about 24 h at room temperature, giving boric acid as one of the products.[895] With dimethyl sulphoxide, on the other hand, no reduction occurs and the B$_2$H$_6$ is cleaved asymmetrically to give [BH$_2$(Me$_2$SO)$_2$]$^+$[BH$_4$]$^-$.[429] Sulphones RR′SO$_2$ do not react.[442]

Except in the case of fluorine monoxide F$_2$O (p. 134), there is no information regarding the manner in which diborane(6) reacts with compounds containing oxygen linked to a halogen.

REACTIONS WITH COMPOUNDS OF SULPHUR, SELENIUM AND TELLURIUM

There are no reports of any studies concerning the behaviour of diborane(6) with elementary sulphur, selenium or tellurium.

With hydrogen sulphide diborane(6) forms no adduct even at -78°C but undergoes a very slow reaction to produce a glassy polymer which has a formula that deviates somewhat from (HBS)$_x$.[395] Since thiohydrolysis does not occur, the behaviour is quite unlike that with water. But under anhydrous conditions in tetrahydrofuran, lithium hydrogen sulphide reacts with diborane(6) below 0°C to produce two ionic species[428], HSBH$_3^-$ and



Diborane(6) reacts with the ion HSBH$_3^-$ to produce a third ionic species, HS(BH$_3$)$_2^-$ [454] (p. 88), and the same species is produced on reaction with other base analogues that give rise to the hydrosulphide ion SH$^-$ in liquid H$_2$S.[690, 557–8] This has a low stability in solution, and it readily loses hydrogen to give products which have not been fully characterized. It would, however, be expected that the decidedly labile μ- mercaptodiborane(6) HSB$_2$H$_5$ is one of them, since this compound is certainly produced on the introduction of hydrogen chloride[557–8] (p. 197).

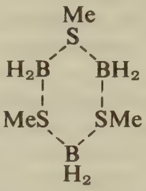
It has been shown in a study of sulphur-boron bonding[395] that the power of the sulphur to form coordinate links to boron is enhanced as the hydrogen atoms on the sulphur are replaced by methyl groups. Thus it is just possible to demonstrate that methyl mercaptan forms the adduct HMeS.BH$_3$ with diborane(6) at -78°C[395], while dimethyl sulphide gives the more stable adduct Me$_2$S.BH$_3$[395, 803], which can be isolated as a solid below its melting point of -38°C.

$$Me_2S + \tfrac{1}{2}B_2H_6 \rightleftarrows Me_2S.BH_3$$

This adduct has a greater stability than that formed by dimethyl ether, and it is generally true that organic sulphides give stronger coordinate bonds with borane(3) than their oxygen analogues.[881] One consequence of this is that diborane(6) is much more soluble in organic sulphides than in ethers[194] (cf. the parallel trend in the strengths of the coordinate bonds formed with BH$_3$ by phosphines and amines respectively, p. 118).

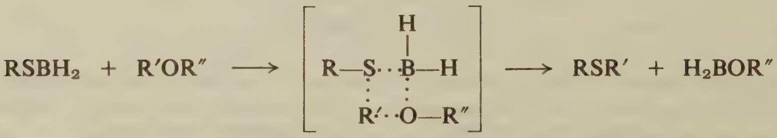
Other than undergoing reversible dissociation, the adducts of dialkyl sulphides R$_2$S.BH$_3$ are unchanged by mild heating, whereas the mercaptan adducts HRS.BH$_3$

readily lose hydrogen, as do mixtures of mercaptans and diborane(6).[896] Thus when R = methyl, a polymer of formula $(MeSBH_2)_x$ is obtained, and on heating this *in vacuo* it is partially converted to volatile oligomers.[395] Alternatively the solid may be dissolved in tetrahydrofuran, when it is converted to the cyclic trimer[896]



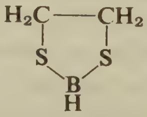
The corresponding cyclic trimer $(EtSBH_2)_3$ appears to be the most stable form in the case of the ethyl analogue, since it is spontaneously formed from the polymer at 25°C.[559] However, on heating the trimer of the methyl analogue the vapour density corresponds to a molecular weight lower than that of the trimer, and at 140°C accords approximately with that of the dimer[395]; but the compound decomposes further to give tris(methylthio)borane(3) $(MeS)_3B$ as one of the products, and this product on heating with more of the trimer $(MeSBH_2)_3$ undergoes a redistribution reaction to produce bis(methylthio)borane(3)[897] which is associated through coordinate sulphur bonding rather than hydrogen bridging (p. 98). At about 90°C, the oligomers of $MeSBH_2$ react with more diborane(6) to give the unstable μ-methylmercaptodiborane(6)[395, 559], which is described on p. 97. A great variety of products are thus obtainable from diborane(6) and mercaptans. Under other conditions, polyboron-sulphur compounds of unforeseen stability result.[738]

The covalent B—S bonds in the alkylthio-substituted boranes are not so strong as the covalent B—O bonds in the alkoxy derivatives of BH_3. Further, there is evidence that the strength of the B—O bond exceeds that of the B—S bond by an amount greater than that by which the C—O bond exceeds the C—S bond in strength. If this were not so, it would be difficult to explain the fact that alkylthioboranes will cleave ethers to give thioethers[893], a reaction which apparently occurs via a 4-centre reaction complex:



$$RSBH_2 + R'OR'' \longrightarrow \left[\begin{array}{c} H \\ | \\ R{-}S\cdots B{-}H \\ \vdots \quad \vdots \\ R'\cdots O{-}R'' \end{array}\right] \longrightarrow RSR' + H_2BOR''$$

The reaction of diborane(6) with 1,2-ethanedithiol $HSCH_2CH_2SH$ has been studied. Hydrogen is liberated and, according to the ratio of the reactants, thioboranes with chainlike and ring structures, i.e. $H_2BSCH_2CH_2SBH_2$, $(CH_2S)_2BH$ and $(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$, are obtained in varying proportions; but on account of additional boron-sulphur coordinate bonding these substances are not monomeric in the condensed state.[564] The second of these is however monomeric in the vapour phase and has a 5-membered ring structure:



1,3,2-dithiaborolane

Disulphanes also react with B_2H_6. Thus dimethyldisulphide MeSSMe gives the same product as the mercaptan MeSH, namely $(MeSBH_2)_x$.[395] The preservation of the C—S bonds is however not invariably observed, either with disulphanes or thiols, since with the triphenylmethyl derivatives $Ph_3CSSCPh_3$ and Ph_3CSH cleavage of the C—S bond occurs to give the products Ph_3CH and $(HBS)_x$.[606] But in general thioethers possess a stability towards diborane(6)[500], and form at most weak adducts from which the reactants can be recovered unchanged. Nevertheless C—S bonds are frequently ruptured when the sulphur is attached to an unsaturated organic residue, as with certain thioketals[898]; but even this is not a reliable guide, since the C—S bonds in allyl methyl sulphide and allyl phenyl sulphide are reported to be left intact by B_2H_6.[642, 899] It appears that C—S bond rupture occurs only when the esteric conditions permit B←S coordination and a subsequent hydride shift, but the matter cannot be said to be fully understood.[898]

In the presence of an ether, diborane(6) reacts with a thiol in a different way, transferring an alkyl group of the ether to the sulphur, thus forming a new C—S bond.[893]

Organic sulphides containing other donor atoms such as nitrogen or phosphorus, e.g. Me_2NCH_2SMe and Me_2PCH_2SMe, form borane(3) adducts with B_2H_6, but in the mono adducts the BH_3 group appears not to be linked to the sulphur; no bis adduct is reported for the phosphorus compound, but boron-sulphur bonding occurs in the bis adduct of the nitrogen compound.[771] This is an unstable liquid which decomposes spontaneously at room temperature by a hydride shift:

$$H_3B.NMe_2CH_2S(Me).BH_3 \rightarrow H_3B.NMe_3 + \frac{1}{n}(MeSBH_2)_n$$

The substituted sulphonium ylide $Me_3SiCH{=}SMe_2$ or $Me_3Si\bar{C}H{-}\overset{+}{S}Me_2$ readily forms a borane(3) adduct with B_2H_6 in ether solution, but the adduct is unstable and liberates dimethyl sulphide even at low temperatures to leave an unidentified mixture of boron compounds.[411]

Knowledge regarding the behaviour of diborane(6) with compounds containing sulphur attached to elements other than carbon is limited. When it is attached to boron, as in alkylthioboranes $(RS)_3B$ or $(RS)_2BR'$, reversible exchange of the alkylthio group RS for hydrogen occurs, presumably to give compounds such as $BH(SR)_2$.[480] In this there is a parallel with the alkoxyboranes $(RO)_3B$ and $(RO)_2BR'$. It is to be expected that the selenium and tellurium analogues $(RSe)_3B$ and $(RTe)_3B$—which have more recently been prepared[565–7]—will behave similarly to give the unknown compounds of types $(RSe)_xBH_{3-x}$ and $(RTe)_xBH_{3-x}$ $(x=1, 2)$, but the matter has not been put to experimental test.

When the sulphur is linked to nitrogen, diborane(6) effects the formation of a mono adduct only, with the boron here apparently linked to the sulphur, as when a methylthiodialkylamine $MeSNR_2$ is converted initially to the adduct $Me(R_2N)S.BH_3$.[900] Such adducts are however unstable and undergo a hydride shift spontaneously at room temperature to give dialkylamine methylthioboranes $HR_2N.BH_2SMe$. Bisdimethylamino sulphide $(Me_2N)_2S$ again gives only the monoadduct $(Me_2N)_2S.BH_3$, which, though slightly more stable, undergoes a similar hydride shift to form the dimethylamino sulphide $(Me_2N)_2S$ again gives only the mono adduct $(Me_2N)_2S.BH_3$, adjacent nitrogen is to increase the donor power of the sulphur towards borane(3), and this has been ascribed to stabilization through sulphur-nitrogen d_π–p_π interaction.[524]

The behaviour of diborane(6) towards certain compounds in which sulphur is linked to oxygen by a double bond has been examined. Dimethyl sulphoxide Me_2SO does not give a simple borane(3) adduct, but cleaves the B_2H_6 asymmetrically to give the ionic compound $[BH_2(OSMe_2)_2]^+BH_4^-$, even at low temperatures.[429] The solid product is soluble in dichloromethane. It has not been determined whether the sulphur or oxygen of the ligand is linked to the boron in the cation, but since sulphones $RR'SO_2$ on the other hand do not react with diborane(6)[442], this would suggest that in the case of dimethyl sulphoxide the lone pair of electrons on the sulphur atom is responsible for the bonding. Sulphur dioxide destroys diborane(6) slowly at room temperature when admixed with it, the reaction producing H_2S, sulphur and boric acid.[895] The time required for the complete decomposition is about 24 h, but in the presence of certain solvents such as ether the reaction is much more rapid and occurs at low temperatures.

In flash photolysis of the mixture, however, hydrogen, boron sulphide B_2S_3 and a polymer of formula $(HBS)_x$ have also been identified among the products.[901]

No information is available concerning the reaction of diborane(6) with compounds containing sulphur-halogen bonds.

Very little is known about the behaviour of diborane(6) with compounds of selenium and tellurium. That these elements can form covalent bonds with boron is witnessed by the existence of μ-methylselenodiborane(6) $MeSeB_2H_5$[1004], in addition to tris(alkylseleno)- and tris(alkyltelluro)-boranes, $(RSe)_3B$ and $(RTe)_3B$, as mentioned above (p. 131). Such other cyclic selenoboron compounds as are known[902–3, 567] do not require diborane(6) for their formation.

REACTIONS WITH HALOGENS AND THEIR COMPOUNDS

Diborane(6) reacts with the halogens and many of their compounds, but the number and variety of boron-containing products are more restricted than for the products obtained from reactions with compounds of group-V and group-VI elements. A key to the behaviour of diborane(6) with the halogens is provided by the strengths of the boron-halogen bonds, which are given for the boron trihalides in Table XVII. Not only are these in every case stronger than the corresponding carbon-halogen bonds, but the overall spread is much greater. Thus the B—F bond with a bond energy of 154·3 kcal mol^{-1}, compared with a C—F bond energy in CF_4 of 117·0 kcal mol^{-1}, is the strongest usually written as a single bond that is known to chemistry. It must however be conceded that its order doubtless exceeds unity through a measure of π bonding, which effect becomes progressively less important as the atomic number of the halogen increases. The overall effect is that B—F bonds show the greatest stability and B—I bonds the greatest reactivity in the series: indeed, boron shows a very exceptional affinity for the first-row element fluorine, which is greater even than the remarkable affinity which it manifests in covalent bonding for oxygen, this in turn being greater than its marked affinity for nitrogen. Its affinity for iodine is however distinctly low, and BI_3 is an endothermic compound.[155]

Table XVII.—Boron-Halogen Bond Energies in the Boron Trihalides

Halide BX_3	B—X bond energy(a)	
	kcal mol^{-1}	kJ mol^{-1}
BF_3	154·3	645·6
BCl_3	106·1	443·9
BBr_3	88·0	368·2
BI_3	63·7	266·5

(a) Calculated from thermochemical data in Refs. 155 and 190.

Even in the absence of definite information on the subject in the open literature, there is scarcely room for doubt that elementary fluorine will react spontaneously with diborane(6) down to exceedingly low temperatures, as it does with hydrogen and many hydrides. Diborane(6) certainly ignites in 'flox' (a mixture of oxygen and fluorine) at −195°C[904], and the combination has been tested as a rocket propellant. It has long been known that at ordinary temperatures chlorine reacts explosively with diborane(6), with the separation of some elementary boron, but that the reaction can be moderated by reducing the temperature. Under such conditions and with chlorine in excess, the reaction proceeds quantitatively according to the equation[269]

$$B_2H_6 + 3Cl_2 \rightarrow 2BCl_3 + 6HCl$$

Even with diborane(6) in excess the products are essentially the same and most of the excess is recovered unchanged with only a little of the partially halogenated product

B_2H_5Cl. By contrast, bromine attacks diborane(6) only very slowly at room temperature, even in the presence of light, and several hours at 100°C are required to complete the reaction.[269] The main product is BBr_3, but B_2H_5Br can be isolated in appreciable amounts. Iodine does not react with pure B_2H_6 at room temperature, even after several days[905], but B_2H_5I is very slowly formed on heating.[573] The BI_3 and unidentified oily products originally reported[572] probably arise secondarily by interaction with the decomposition products of diborane(6) after excessively prolonged standing or on heating. In the presence of a trialkylamine or an ether, however, iodine reacts with diborane(6) to produce iodoborane(3) adducts such as $Me_3N.BH_2I$[906] and $Et_2O.BH_2I$[430], and reaction may proceed further.

The behaviour of diborane(6) with the hydrogen halides is of interest. Unfortunately the interaction with anhydrous HF has not been reported. With gaseous HCl no reaction with B_2H_6 is observed at room temperature, even in the presence of $AlCl_3$.[319] However, if B_2H_6 containing HCl is allowed to stand for 3 months the HCl is consumed with the formation of a variety of products, not merely chlorodiborane(6) B_2H_5Cl; but if the mixture is heated to 120°–130°C much of the diborane(6) is converted to B_5H_9.[270] By contrast, diborane(6) readily reacts at 80°–90°C with HBr in the presence of $AlBr_3$ as a catalyst, giving the bromo derivative B_2H_5Br[319], whereas with HI a corresponding reaction occurs at 50°C without a catalyst[572–3]:

$$B_2H_6 + HI \rightarrow B_2H_5I + H_2$$

However, in the presence of an ether or an amine, hydrogen halides give adducts of halogenoboranes, e.g. $R_2O.BH_2Cl$ or $R_nH_{3-n}N.BH_2Br$.[906] The halogenodiboranes B_2H_5X very readily disproportionate to B_2H_6 and BX_3, although the stability increases from the chloro to the iodo compound. The reaction is reversible, so that diborane(6) will also react with the boron trihalides.

With boron trifluoride, there is only one isolable intermediate, namely BHF_2[907, 568]:

$$B_2H_6 + 4BF_3 \rightleftharpoons 6BHF_2$$

The reaction is catalyzed by ether, methanol or BCl_3.[908] Fluorodiborane(6) B_2H_5F is unknown and apparently not isolable. It is rather surprising that BHF_2 was not reported before 1964; indeed, no partially substituted halogen derivative of BH_3 was isolated before 1959. Other methods of producing BHF_2 are now known, such as heating B_2H_6 with an organofluoroborane(3), or preferably by reacting BF_3 with $BH(OMe)_2$.[907] The infra-red[907, 909–11] and n.m.r.[907, 912] spectra of BHF_2 and isotopic species have been reported. The molecule has also been the subject of theoretical studies.[913–14] It is not very stable, but disproportionates over a period of weeks to BF_3 and B_2H_6.[908]

With BCl_3 diborane(6) gives two products, chlorodiborane(6) B_2H_5Cl and dichloroborane(3) $BHCl_2$[317, 568, 570, 915], by the reversible reaction

$$B_2H_6 + BCl_3 \rightleftharpoons B_2H_5Cl + BHCl_2$$

Traces of BH_2Cl are detectable from spectral bands in the gaseous mixtures[578], but this species has never been isolated. That dichloroborane(3) $BHCl_2$ escaped identification by a number of expert workers in the field over several decades is probably to be attributed to the exceedingly difficult separation from BCl_3 and B_2H_5Cl by conventional vacuum fractionation. Its first isolation was realized from the products of heating BCl_3 with hydrogen[916], and it is also a principal product of heating BCl_3 with methane.[308] The spectra of $BHCl_2$ and its isotopic species have been reported[308, 569, 916–19], as have the thermodynamics of disproportionation[914]; this reaction requires a few weeks for completion in a closed cell at room temperature. In the B_2H_6-BCl_3 distribution equilibrium the concentration of the intermediate B_2H_5Cl is favoured at room temperature, but that of $BHCl_2$ is favoured at 100°C.[570]

In a comparable manner, diborane(6) equilibrates with BBr_3 to give B_2H_5Br and $BHBr_2$.[571, 568] The dibromo compound $BHBr_2$ can also be formed by heating BBr_3 with hydrogen.[325] Its spectrum[920–1] and that of $BDBr_2$[922] have been reported. On the other hand, diiodoborane BHI_2 is unknown and, unlike B_2H_5I, did not appear in a study of the B_2H_6-BI_3 system.[573] Rather, diborane(6) reacts with boron triiodide according to the overall equilibrium reaction

$$5B_2H_6 + 2BI_3 \rightleftharpoons 6B_2H_5I$$

and B_2H_5I is the only isolable intermediate.

In the presence of a trialkylamine, the product of reacting B_2H_6 with a boron trihalide may be the amine halogenoborane(3), e.g. $R_3N.BH_2Br$ or $R_3N.BHBr_2$.[906] Although the monohalogenoboranes BH_2X cannot be isolated either as monomers or dimers, presumably because they disproportionate too rapidly, there is every reason to believe that they occur as intermediates in B_2H_6-BX_3 redistribution reactions, and there is the above-mentioned spectroscopic evidence in the case of the chloro compound BH_2Cl.[578] But, like the dihalogeno compounds BHX_2, the above example shows that they can be stabilized by coordination: thus ethers give complexes such as $R_2O.BH_2Cl$[923-4] and $Et_2O.BH_2I$[924, 430], while amines give well characterized complexes such as $R_3N.BH_2X$[925] and $C_5H_5N.BH_2I$[926] recognizable by their infra-red and n.m.r. spectra.

With diboron tetrachloride B_2Cl_4 at or below 0°C, diborane(6) effects rupture of the B—B bond, at least in part: a complex mixture of products results.[318, 578]

Our knowledge of the behaviour of diborane(6) with other halogen compounds is sparse indeed. Although it is commonly assumed, at least tacitly, that halogen linked to carbon is inert towards B_2H_6, no systematic study of the matter has been undertaken, and it is certainly not universally true. Thus it is definitely known that the chlorine in acid chlorides is reactive towards diborane(6) and is eliminated, since the products are simply alcohols.[632-3] Still more to the point is the conversion at 15°C in nitromethane solvent of aralkyl chlorides and bromides to the corresponding hydrocarbon.[607] Certainly the conversion of halides to hydrocarbons by diborane(6) is generally thermodynamically favoured, expecially in the case of the fluorides, and future studies should be directed towards determining the heights of kinetic barriers. Other cases involving rupture of carbon-halogen bonds will doubtless be found, because alkali metal tetrahydroborates, which are in general to be regarded as weaker hydrogenating reagents than diborane(6), are known to remove halogen from a number of organic substances[383], including vinyl and allyl bromides[927], vinylic fluorides and chlorides[928], and halogenated hydrocarbons[929], whereas dehalogenation of CBr_4 and CHI_3 by $NaBH_4$ is only partial.[930] Although one would suspect that many similar dehalogenation reactions would also occur with diborane(6), the reaction paths and even the products may not necessarily be the same in all cases, and frequently fluorine compounds might well react differently from those of the other halogens.

Concerning the behaviour of diborane(6) with halogen covalently bound to nitrogen, limited information is available only for the halides NF_3, N_2F_4 and Me_2NCl (see pp. 117 and 114). In the case of compounds containing halogen linked to a group-VI element, only the compound OF_2 appears to have been subjected to test. Here reaction sets in slowly at −195°C and becomes violent at higher temperatures.[931, 904] The B_2H_6-OF_2 system has been seriously considered recently as a propellant suitable for future unmanned long-distance interplanetary spacecraft.[932-6] The kinetics of the reaction have been studied.[937-8] The products are BF_3, B_2O_3 and H_2, but in the reaction conducted at 300–330 K small quantities of BHF_2, B_2F_4 and unidentified boron-containing solids have been observed.

REACTIONS FORMING CARBORANES

Unlike the higher boranes, diborane(6) has found comparatively little use in the production of carboranes, probably because carboranes normally contain more than two boron atoms per molecule, so that a preformed boron skeleton is helpful in obtaining appreciable yields. However, the first evidence for the existence of carboranes was provided in 1953 from experiments in which a hot wire was used to flash B_2H_6 admixed with acetylene.[939] Very small yields of volatile compounds containing two carbon atoms and respectively three, four and five boron atoms suggested the existence of molecules of formulae $C_2B_3H_x$, $C_2B_4H_y$ and $C_2B_5H_z$, as well as a number of other new compounds. Better yields of products since identified as the *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$ have been formed by passing an electric discharge through B_2H_6-C_2H_2 mixtures at reduced pressure, with or without dilution by an inert gas such as helium.[940, 381] Methylated derivatives are formed at the same time.

Substituted carboranes can also be formed from alkyldiboranes. Thus 1,5-dimethyl-2,3,4-triethyl-1,5-dicarba-*closo*-pentaborane appears in a yield of 10–15%, together with derivatives of other carboranes, when ethyldiboranes are heated with acetylene.[941–2] Alternatively ethyldiboranes may be heated with alkynylboranes, when the yield of substituted 1,5-dicarba-*closo*-pentaboranes may exceed 50%.[943] A rather similar mixture of substituted carboranes is formed in about 15% yield when ethyldiboranes are heated with metallic sodium[944], while lithium acts similarly but gives a lower yield; and even when pyrolyzed alone at 200°–230°C ethyldiboranes give detectable quantities of substituted carboranes, including various alkylated dicarba-*closo*-heptaboranes. Although the mechanisms of such reactions are not clear, it has been assumed that they are dependent on the initial formation of $R_2B^{\cdot}$ radicals.[944–5] Since alkyldiboranes are directly preparable *in situ* from diborane(6) and trialkylboranes, these reactions may be regarded as indirect reactions of B_2H_6 itself.

One further synthetic use of B_2H_6 is in the conversion of one carborane into a second carborane containing a greater number of boron atoms. Thus, adopting recommended nomenclature[946], C,C′-dimethyl-*arachno*-dicarbanonoborane $C_2B_7H_{11}Me_2$ is converted at 200°C in diphenyl ether solvent by B_2H_6 mainly into the C,C′-dimethyl-*closo*-carboranes 1,6-$C_2B_8H_8Me_2$ (41% yield) and 1,7-$C_2B_{10}H_{10}Me_2$ (8% yield).[947] It is to be noted that these are pyrolyzing conditions

The general chemistry of these and similar compounds is to be found in the section on the carboranes (p. 450).

Reaction Mechanisms

THE CONVERSION OF DIBORANE(6) TO HIGHER BORANES

The first reported attempts to elucidate the mechanism of interconversion of diborane(6) and other boranes date from 1951[161, 146], when it was established that the rate-determining step in the pyrolysis of B_2H_6 has the kinetic order 1·5 and is associated with an activation energy of *c.* 27 kcal mol^{-1}. During the next decade further detailed investigations of the mechanism of interconversion of the boranes were reported by various workers.[948–53] Since 1961 further relevant publications have been too numerous for more than the essential findings to receive mention here. In nearly every study the mechanistic conclusions were based on the assumption that the initial step is a reversible one, namely

$$B_2H_6 \rightleftharpoons 2BH_3$$

whereas, as has already been seen (pp. 9 and 64), there are serious reasons for doubting the existence of the back reaction, which has never been observed. Other objections to the equilibrium as a basis of the reactions of diborane(6) have been published.[26] Not only is there evidence, arising by implication from the recent electron-impact work described on p. 65, that an appreciable activation energy may be associated with the back reaction, but it is clear that under ordinary pyrolysis conditions no significant or even detectable equilibrium concentration of BH_3 ever becomes established. Accordingly, the BH_3 molecules must be mopped up as fast as they are formed—and at nearly every collision—by some other process; the only satisfactory candidate for this is the process $BH_3 + B_2H_6 \rightarrow B_3H_9$, which is presumably exothermic and must certainly have a low activation energy. This does not imply that triborane(9) B_3H_9, once formed, inevitably becomes part of a stable higher borane such as B_4H_{10} or B_5H_{11}, since it must be concluded that the process $2B_3H_9 \rightarrow 3B_2H_6$ is also exothermic with a low or negligible activation energy, in that B_3H_9 is not isolable. Yet B_3H_9 is thermodynamically stable relative to $B_2H_6 + BH_3$, from which it follows that the process

$$2B_2H_6 \rightarrow B_3H_9 + BH_3$$

will require less energy than the simple unimolecular dissociation $B_2H_6 \rightarrow 2BH_3$, and will therefore become the predominant initial step in the bimolecular region (i.e. under ordinary experimental conditions).

Several different mechanistic schemes based on limited evidence have been advanced at various times for the subsequent production of a number of the isolable higher boranes. However, so much mechanistic evidence of the most varied kind has collected since 1951, that there was a need to examine this complex problem afresh and to derive a single unified mechanism which is in harmony with all the known experimental facts, including those from isotope studies and co-pyrolysis work. With the formation of triborane(9) as the initial step and the ultimate formation of decaborane(14) in mind, the mechanism of the pyrolysis of B_2H_6 can be described in detail by the following scheme, in which the non-isolable fragments B_3H_7 and B_4H_8 play an important and largely unexpected role[18]:

(1) $2B_2H_6 \rightleftarrows BH_3 + B_3H_9$
(2, 3) $BH_3 + B_2H_6 \rightleftarrows B_3H_9 \rightleftarrows B_3H_7 + H_2$
(3*a*) $2B_3H_9 \rightarrow 3B_2H_6$
(4) $BH_3 + B_3H_7 \rightleftharpoons B_4H_{10}$
(5, 8) $B_2H_6 + B_3H_7 \rightarrow BH_3 + B_4H_{10} \rightleftarrows B_5H_{11} + H_2$
(6) $B_3H_9 + B_3H_7 \rightarrow B_2H_6 + B_4H_{10}$
(7) $2B_3H_7 \rightarrow B_2H_6 + B_4H_8$
(7*a*) $2B_3H_7 \rightarrow B_6H_{12} + H_2$
(9) $B_3H_9 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11} + H_2$
(10) $B_3H_7 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11}$
(11) $H_2 + B_4H_8 \rightarrow B_4H_{10}$
(12) $BH_3 + B_4H_8 \rightleftharpoons B_5H_{11}$
(13) $B_3H_9 + B_4H_8 \rightarrow B_2H_6 + B_5H_{11}$
(14) $B_3H_7 + B_4H_8 \rightarrow B_2H_6 + B_5H_9$
(15, 17) $2B_4H_8 \rightarrow B_3H_7 + B_5H_9 \rightarrow B_2H_6 + B_6H_{10}$
(15*a*) $2B_4H_8 \rightarrow B_2H_6 + B_6H_{10}$
(16) $B_4H_8 + B_5H_{11} \rightarrow n\text{-}B_9H_{15} + 2H_2$
(18, 22) $B_4H_8 + B_5H_9 \rightarrow B_3H_7 + B_6H_{10} \rightarrow n\text{-}B_9H_{15} + H_2$
(19) $B_6H_{12} \rightarrow BH_3 + B_5H_9$
(20) $B_3H_7 + B_6H_{12} \rightarrow B_4H_8 + B_5H_{11}$
(21) $B_4H_8 + B_6H_{12} \rightarrow B_5H_9 + B_5H_{11}$
(23) $B_4H_8 + B_6H_{10} \rightarrow 2B_5H_9$
(24) $B_8H_{12} \rightarrow B_6H_{10} + B_2H_2$ (polymerizes)
(25) $BH_3 + B_8H_{12} \rightleftharpoons n\text{-}B_9H_{15}$
(26) $B_3H_9 + B_8H_{12} \rightarrow B_2H_6 + n\text{-}B_9H_{15}$
(27) $B_3H_7 + B_8H_{12} \rightarrow B_2H_6 + B_9H_{13}$
(28) $B_3H_7 + B_9H_{13} \rightarrow B_2H_6 + B_{10}H_{14}$

In this scheme the equations are numbered (in the left-hand column) according to the most complex reactant in increasing boron content and in decreasing hydrogen content for species with the same number of boron atoms. This arrangement broadly corresponds with the order in which the various species appear during the pyrolysis, although it is likely that B_6H_{12} precedes B_5H_9, and $n\text{-}B_9H_{15}$ precedes B_8H_{12}.

All the species in the above mechanism except for B_5H_9 are icosahedral fragments. Other non-icosahedral species are known, such as the molecules $(B_4H_9)_2$ and $(B_5H_8)_2$, but where these occur in the pyrolysis of B_2H_6 they are produced at most in very small yields in side reactions. Recently a number of new non-icosahedral species have been identified in the co-pyrolysis of B_2H_6 and B_5H_9, which latter species is itself one of the pyrolysis products of B_2H_6.[673]

The rate-controlling step in the above scheme is reaction (3), and since $[B_3H_9] \propto [B_2H_6]^{1 \cdot 5}$, the expected order is 1·5 with respect to diborane(6), in agreement with observation. Also the rate of conversion of diborane(6) at any given temperature depends on the ambient concentration of B_3H_9, and the overall kinetic parameters are unaffected by the manner in which B_2H_6 is converted to B_3H_9. The non-isolable species in this mechanism are BH_3, B_3H_9, B_3H_7, B_4H_8 and B_9H_{13}, but there is sound evidence for the transitory existence of all of them[18], and it is seen to be largely through the agency of the first four of these that the higher boranes are synthesized. Although all the other species occurring in the mechanism are isolable, those with 6, 8 and 9 boron atoms are so much less stable than B_5H_9 and $B_{10}H_{14}$ that—except occasionally for B_6H_{10}, depending on the conditions—they do not normally accumulate in sufficient concentration to appear in visible amounts when B_2H_6 is pyrolyzed alone. Instead they require special isolation techniques, in which one of the intermediate boranes is allowed to react with more B_2H_6, usually under pyrolyzing conditions.[954, 17, 673]

All the borane species in the mechanism other than BH_3 and B_2H_2 may be grouped in two classes, namely hydrogen-rich boranes of general formula $(BH)_n(BH_3)_3$ and hydrogen-poor boranes of type $(BH)_n(BH_3)_2$, where n is an integer or zero. Although the former class includes the thermally less stable boranes, with the exception of B_3H_9 its various members do not react readily with one another, probably because they are saturated species. But the hydrogen-poor series, with the possible exception of the non-icosahedral B_5H_9, must be regarded as less saturated and apparently able to interact readily with molecules of either class, that is, in processes associated with low or very low activation energies. They usually react by exchanging BH or BH_3 (but never BH_2) groups, or occasionally by condensation reactions in which a molecule of hydrogen is liberated. Examples of exchange processes are reactions (10) and (13); condensation processes are represented by reactions (*7a*) and (16). The exceptionally low reactivity of $B_{10}H_{14}$ may be due to stereochemical factors. The hydrogen-rich species can undergo fission by splitting off BH_3 rather easily and often reversibly, as in reactions (−2), (−4), (−12), (19) and (−25) [a minus sign denotes a reaction proceeding from right to left]; but with the exception of B_3H_9 in reaction (3), none of the species produced by the pyrolysis of B_2H_6 splits off molecular H_2 in a unimolecular step. The hydrogen-poor species, including diborane(6) itself, cannot do this, and since the only member of this series to undergo unimolecular fission at moderate temperature is B_8H_{12}, which gives B_6H_{10}[17], the species shed here must be B_2H_2, which is observed only as the reported yellow solid polymer. The fact that B_2H_2 polymerizes even at low temperatures is not surprising, in view of its exceedingly unsaturated nature. The reason for the exceptional release of B_2H_2 by B_8H_{12} is probably a structural one, in that its boron skeleton corresponds to the pentagonal pyramid pertaining to B_6H_{10} with two additional linked boron atoms appended to the base.[19] It must be presumed that it is this pair of boron atoms that is cast off, whereas a structure that has only one boron atom in excess of the B_6H_{10} skeleton, i.e. B_7H_{11}, appears to be devoid of stability, since in the latest work[955] no B_7 hydride could be detected even with the mass spectrograph. The conversion of *n*-B_9H_{15} to $B_{10}H_{14}$ does not occur directly, but proceeds via B_8H_{12}, as indicated by the results of isotope studies.[955] Another interesting feature revealed by isotope studies is that when, while undergoing pyrolysis, B_2H_6 converts B_5H_9 to $B_{10}H_{14}$, half of the boron in the latter comes from the pentaborane(9) and the remainder from the diborane(6).[348–9]

A point on which various workers have disagreed is whether B_4H_{10} or B_5H_{11} is the first isolable intermediate to be formed in the decomposition of diborane(6). Since, in the presence of hydrogen, they are interconverted[670] by reaction (8) much more rapidly than either B_2H_6 or B_5H_9 undergoes pyrolysis, experimental proof is difficult. The foregoing mechanism implies that B_4H_{10} appears first, unless reactions (5) and (8) can be written as the single step

$$B_2H_6 + B_3H_7 \rightleftharpoons B_5H_{11} + H_2$$

A gas-chromatographic study of the progress of B_2H_6 pyrolysis at 111°C[956], produced what appeared to be strong evidence that B_5H_{11} is the only borane formed initially, thus supporting a view advanced by various other investigators, both before and since. However, one worker[957] has insisted that B_4H_{10} appears first, arguing principally on the grounds that B_4H_{10} is the main product of pyrolysis of B_2H_6 at 120°C in a hot-cold reactor[342], in which the compound is frozen out as soon as it is formed. This view has received a measure of support from mass-spectroscopic studies[352], in which it was observed that peaks from B_4 species could be produced from pyrolyzing B_2H_6 under conditions of relatively low temperatures and high pressures where those from B_5 species were still absent.

The weight of present evidence therefore supports the latter view, that B_4H_{10} is produced before B_5H_{11}, and that reactions (5) and (8) are separate steps. The gas-chromatographic evidence[956] can be reconciled with this conclusion on reflection that the reversible reaction (8) is fast relative to reaction (3) and that the pseudo-equilibrium between B_4H_{10} and B_5H_{11} is progressively displaced in favour of B_4H_{10} by the increasing concentration of H_2, which is not measured in the gas chromatograph. The maximum concentration for B_4H_{10} would therefore in any case occur later than that for B_5H_{11}.

The subsequent conversion of B_5H_{11} to B_5H_9 is irreversible; but it is not simple and does not occur by the unimolecular process $B_5H_{11} \rightarrow B_5H_9 + H_2$, as has sometimes been supposed. Pentaborane(9) is exceptional in not being an icosahedral fragment and in having a stability higher than that of most boranes; thus once it has been formed, a higher temperature is required to pyrolyze it. There are seen to be two principal routes from B_5H_{11} to $B_{10}H_{14}$: (*a*) a low-temperature route that does not involve B_5H_9 and utilizes steps (16), (−25), (27) and (28); and (*b*) a high-temperature route that passes through B_5H_9 and is composed of reactions (−12), (14), (17), (22), (−25), (27) and (28). The evidence for this has been discussed in detail.[18] The overall mechanism previously described is believed to be in harmony with all established experimental observations to date regarding the conversion of B_2H_6 to higher boranes.

Deuterodiborane B_2D_6 decomposes much more slowly[341] than B_2H_6; the activation energy is about 4·8 kcal mol^{-1} higher[958], as determined from deuterium evolution.

ISOTOPE-EXCHANGE MECHANISMS WITH DEUTERIUM AND OTHER BORANES

It was initially observed that hydrogen exchange between B_2H_6 and D_2 is conveniently measurable below 75°C and that the order is 1·5 with respect to $[B_2H_6]$ and 1 with respect to $[D_2]$ at low pressures of deuterium, changing to zero order at higher pressures.[959] After the data had been reinterpreted[960], a third interpretation[372] provided an explanation of the exchange in terms of the reversible reaction (3) in the interconversion mechanism discussed on p. 136. This being so, the deuterium atoms will enter the diborane(6) molecule in pairs, and the mixed molecular species HD will not be formed in the very early stages. However, the matter does not appear to have been tested experimentally, although in studies with the mixed isotopic molecules HD, HT and DT an inverse isotope effect has been observed.[961] This effect is explained by taking the order of stability of the isotopic species of diborane(6) as $B_2H_5T > B_2H_5D > B_2H_6$ and assuming that the rate-controlling step is the reversible equilibrium by which they are formed, i.e.

$$BH_2D + B_2H_6 \rightleftharpoons B_3H_8D \rightleftharpoons B_2H_5D + BH_3$$

Isotopic self-exchange in B_2H_6-B_2D_6 mixtures again readily occurs with a reaction order of 1·5.[959] By the use of ^{10}B-enriched diborane(6) it was also found that boron exchanges equally easily.[962] Reliance on the step

$$BD_3 + B_2H_6 \rightarrow BD_3BH_3 + BH_3$$

would imply that the ratio of D:^{10}B exchanged should be 3, but by means of a specially designed mass spectrometer coupled to a flow reactor it was shown the ratio was significantly lower.[372] The discrepancy was alternatively explained by the presence of some of the deuterated species $B_3D_3H_6$, for which an isotope effect could exist in its fragmentation, or by a small amount of exchange via the boryl radical BH_2. There are good reasons for neglecting the latter possibility, especially as the former appears quite likely in the light of reaction (1) given in the scheme on p. 136, according to which the most important reaction in the exchange would be

$$B_2H_6 + B_2D_6 \rightarrow B_3D_3H_6 + BD_3 \quad (\text{or } B_3D_6H_3 + BH_3)$$

Exchange of both boron and hydrogen likewise occurs between diborane(6) and pentaborane(11), but the reaction is first-order with respect to B_2H_6 and half-order with respect to B_5H_{11}.[963, 669] Again it appears that BH_3 groups are exchanging via B_3H_9, and that they arise from the pentaborane by virtue of the pseudo-equilibrium

$$B_5H_{11} \rightleftharpoons B_4H_8 + BH_3$$

This conclusion finds support in the observation that B_5H_{11} will exchange alkyl radicals with alkyldiboranes or 1,2-dialkyldiboranes.[461, 459] Again the ratio of D : ^{10}B exchanged departs from the required value of 3, but the explanation in this case is an intramolecular reshuffling in B_5H_{11}, in which the exchange is more rapid for deuterium than for boron. In the liquid phase the boron is completely exchanged within 0·5 h at room temperature.[955]

A completely different situation exists in the exchange of fully deuterated diborane(6) B_2D_6 with either B_5H_9 or $B_{10}H_{14}$. Here, unaccompanied by boron exchange, deuterium enters these higher boranes at the terminal positions only and does not substitute the bridge hydrogen atoms.[669, 964–6] Elevated temperatures (80° and 100°C respectively) are required in order to effect exchange within a few hours. In the former case the order is 0·5 with respect to B_2D_6 and 1 with respect to B_5H_9. The mechanism is thus different from that of the B_2H_6 self-exchange or exchange with B_5H_{11}, and the rate-controlling step is believed to be a bimolecular collision of trideuteroborane(3) BD_3 with B_5H_9, resulting in a simple exchange with one terminal hydrogen atom of the latter. The isotope effect is normal.[961] In this case boron exchange occurs only in the presence of a catalyst[967] or under pyrolyzing conditions.[968, 349] No information is available concerning the mechanism of the exchange of decaborane(14) $B_{10}H_{14}$ with B_2D_6, but it is presumably similar.

Points of similarity are also apparent in the behaviour of B_6H_{10} and B_6H_{12} respectively with B_2H_6, since again neither exchanges boron under conditions where the exchange of hydrogen occurs. However, the temperature required in both cases is much lower. Deuterium exchange between hexaborane(10) B_6H_{10} and B_2D_6 proceeds at −20°C as far as the species $B_6H_5D_5$, in which only the basal terminal hydrogen atoms have been exchanged[969–70]—a result as surprising as it was unpredictable. Deuterium is exchanged between hexaborane(12) B_6H_{12} and B_2D_6 below −30°C, but stops with the substitution of both BH_2 groups at 1,1,4,4-tetradeuterohexaborane(12) $B_6H_8D_4$.[971] At room temperature complete deuteration to B_6D_{12} occurs, but this may be merely the ultimate consequence of the onset of deuterium migration, which was shown to occur with 1,1,4,4-$B_6H_8D_4$ above −30°C.

Two different mechanisms appear to take place simultaneously in the exchange of tetraborane(10) B_4H_{10} with B_2H_6.[972] At least, inasmuch as B_4H_{10} exchanges both hydrogen and boron and also exchanges methyl radicals with the methylated species B_2H_5Me and 1,2-$B_2H_4Me_2$[459], this borane resembles B_5H_{11}, but differs from it in that two competing reactions are occurring and the kinetics are more complex.[669] The reactions are reported to be first order with respect to B_4H_{10}, but of order 0·25 and 0·5 respectively with respect to B_2H_6. For a possible explanation, see p. 224.

MECHANISMS OF OTHER REACTIONS

Apart from the foregoing investigations, very few mechanistic studies have been carried out to date on the exchange reactions of diborane(6). Deuterium exchange between deuterodiborane(6) B_2D_6 and aluminium tetrahydroborate $Al(BH_4)_3$ has been studied.[973] The rate depends on the relative partial pressures in a complex way that suggests that the dissociation of both molecules occurs to produce a common, but isotopically different, borane(3) species. With sodium tridecahydrodecaborate(1−) $NaB_{10}H_{13}$ in ether solution, diborane(6) undergoes complete boron exchange, probably via the $B_{11}H_{16}^-$ ion.[675] Research on the exchange reaction of B_2D_6 with μ-dimethylaminodiborane(6) $B_2H_5NMe_2$ has suggested a mechanism that likewise involves the trideuteroborane(3) molecule BD_3.[733] However, such a mechanism cannot be invoked to explain the observed hydrogen-deuterium exchange between the boron and germanium in mixtures of B_2H_6 and the deuterogermanes GeD_3PH_2[745] or GeD_3AsH_2[746] respectively: here it would appear to be a case of genuine proton exchange.

Few other reactions of diborane(6) have received mechanistic study. The kinetics of the reactions with the species BMe_3[466], C_2H_4[636], NMe_3[756], PH_3[801] and O_2[829–31, 835] have received attention. In most cases it was concluded that BH_3 plays an important role in the mechanism. Preliminary attempts have also been made to elucidate the mechanism of the ternary reaction of B_2H_6 with iodine and ether, in which case asymmetric cleavage of the diborane is involved and intermediates such as the $[BH_2(OEt_2)_2]^+$ ion occur.[430] For a molecule with the reactivity of diborane(6) surprisingly little is known about its reaction mechanisms, and there is clearly much room for further work in this field.

THE IONS $B_2H_6^+$ AND $B_2H_6^-$ AND THE HEXAHYDRODIBORATE(2−) ANION, $B_2H_6^{2-}$

The intensity of the positive ion $B_2H_6^+$ in the mass spectrum of diborane(6)[8–13] is so low, that there was initial difficulty in distinguishing it from background peaks.[7] It is presumably therefore intrinsically of relatively low stability, but the observation of $B_2D_6^+$ [14, 15] confirmed its existence. Its appearance potential and bridge-bond dissociation energy have been approximately determined[74], while knowledge of its electronic states has been gained from photoelectron spectroscopy of diborane(6)[142] and from all-valence-electron CI calculations.[974]

The negative ion $B_2H_6^-$ has not so far been observed as a metastable ion in the negative-ion mass spectra of boranes, nor did it appear in positive-ion-impact studies with diborane(6).[25] However, by photoirradiation of diborane(6) in an argon matrix and by γ-irradiation of adsorbed B_2H_6 on silica gel and other adsorbents at 77 K[975], the electron spin resonance spectra of both $B_2H_6^-$ and $B_2D_6^-$ at 4 K have been obtained.[976] Theoretical studies indicate that an eclipsed ethane-like structure is more stable than a bridged structure.[72] However, $B_2H_6^-$ is apparently the least stable ion in the series $B_2H_x^-$ ($x = 1$–7). In any case, there are good theoretical reasons for expecting B_2H_6 to have a non-zero electron affinity. However, the reported unstable intermediate of empirical formula NaB_2H_6[698] is more probably $Na_2B_4H_{12}$.

The $B_2H_6^{2-}$ anion, if it exists, is isoelectronic with ethane. The products obtained by Stock[691–3] from the slow addition of diborane(6) to sodium, potassium and calcium amalgams were originally assumed to be $Na_2B_2H_6$, $K_2B_2H_6$ and CaB_2H_6. The assumption was later questioned when it was shown by means of X-ray diffraction that $NaBH_4$ could be sublimed from the product of the sodium reaction, and that unidentified material was also obtained.[977] However, it must be noted that this observation was made only after heating, and does not rigidly disprove the existence of $Na_2B_2H_6$ as the initial product in the room-temperature reaction: unlike KBH_4, the initial product from the potassium reaction is insoluble in liquid ammonia.[692]

Later work with sodium amalgam provided strong, if incomplete, evidence for the initial preparation of $Na_2B_2H_6$, at least in the presence of ethers.[698, 978] It appears to be thermally stable at room temperature, but reacts progressively with further diborane(6) in stages, probably according to the scheme

$$2Na + B_2H_6 \xrightarrow{Et_2O} Na_2B_2H_6 \xrightarrow{B_2H_6,\ Et_2O} Na_2B_4H_{12} \xrightarrow[slow]{Et_2O} NaBH_4 + NaB_3H_8$$

The first product was however not isolated in the later work, and further research is required to confirm its identity.

THE ION $B_2H_7^+$ AND THE HEPTAHYDRODIBORATE(1−) ANION, $B_2H_7^-$

Although B_2H_7 has never been observed, the observation of both the ionic species $B_2H_7^+$ and $B_2H_7^-$ raises the question of the capability of existence of the free neutral molecule as a transitory species. If so, it is not obvious whether an asymmetrical doubly bridged or a symmetrical singly bridged structure is likely to be the more stable. A further consideration in favour of its potential existence is that the covalent structure should in any case be thermodynamically more stable than the ion-pair $[B_2H_6^-][H^+]$, which in turn should be more stable than the separated ions.

The ionic species $B_2H_7^+$, mass number 29, occurs in the mass spectra of B_4H_{10} and higher boranes.[12,144,954,979–81] It has also more recently been observed in the low-temperature chemical ionization spectrum of B_2H_6 in methane below 86 K.[76] The proton affinity of B_2H_6 is appreciable (147 ± 4 kcal mol^{-1} [76]), but the stability of $B_2H_7^+$ is not very high with respect to cleavage to $B_2H_5^+ + H_2$, so that any proton-transfer reaction with enough excess energy to decompose the product is useless. In methane it appears that the species $C_2H_9^+$ is responsible for its formation according to the steps

$$CH_4 + CH_5^+ \rightarrow C_2H_9^+$$

$$B_2H_6 + C_2H_9^+ \rightarrow B_2H_7^+ + 2CH_4$$

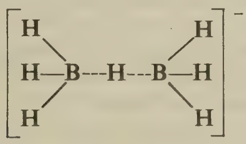
—since at low methane concentrations the production of $B_2H_7^+$ is proportional to the fourth power of the pressure, and not the second power, as would be expected if the species directly responsible were CH_5^+. (Direct interaction of B_2H_6 with CH_5^+ produces $B_2H_5^+$, p. 56. With B_2D_6, the ion $B_2HD_6^+$ is similarly produced. The structure of $B_2H_7^+$ has not been determined. An asymmetrical structure with a 3-centre HBH bond on one boron atom has been proposed.[76] As there are only 6 electron pairs, a more symmetrical structure with a triple hydrogen bridge would demand a very special kind of electron-deficient bonding. There is evidence that the mode of decomposition is by the only slightly endothermic step[76]

$$B_2H_7^+ \rightarrow B_2H_5^+ + H_2$$

The negative ion $B_2H_7^-$ was not found in the negative-ion mass spectra of higher boranes such as tetraborane(10) and pentaborane(9)[16,23], but appeared as a free ionic species when diborane(6) was subjected to positive-ion impact.[25] In an ion-cyclotron-resonance study[80] it has been shown that the mode of formation is by the gas-phase reaction

$$BH_4^- + B_2H_6 \rightarrow BH_3 + B_2H_7^-$$

The heptahydrodiborate(1−) anion $B_2H_7^-$ is readily formed in solution in a polyether or even tetrahydrofuran, in which it has a certain limited stability. Infra-red[982] and ^{11}B n.m.r. studies[50,983–4] on solutions of the sodium salt in polyethers have confirmed the presence of the free anion and show the boron atoms to be equivalent. All the evidence is compatible with a structure containing a single hydrogen bridge



in which rapid tautomerism is occurring. The ^{11}B n.m.r. spectrum alone failed to establish this uniquely, because the expected coupling for the bridge proton is apparently too weak for observation at the resolutions used; however, spin coupling of bridge and terminal hydrogen has been observed in the ^1H spectrum of a fully substituted phosphonium salt.[985] In solution the ion exchanges rapidly with B_2H_6 and more slowly with an excess of the BH_4^- ion.[138] Theoretical treatments based on molecular-orbital, valence-bond, non-paired-spatial-orbital and *ab initio* methods[77, 104, 106, 986–7, 1006] all support the above structure and give various estimates for the bridge-bond dissociation energy

$$B_2H_7^-(g) \rightarrow BH_4^-(g) + BH_3(g)$$

That the lone pair of electrons usually thought necessary for hydrogen-bond formation may here in fact be antibonding in character, finds a measure of support from calorimetric studies.[437]

The sodium salt NaB_2H_7 can be formed in solution by the action of diborane(6) on sodium hydride or sodium tetrahydroborate dissolved in diglyme.[234,238]

$$NaH + B_2H_6 \xrightarrow{\text{diglyme}} NaB_2H_7$$

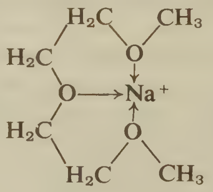
$$2NaBH_4 + B_2H_6 \xrightarrow{\text{diglyme}} 2NaB_2H_7$$

The lithium salt is formed in a comparable manner.[387] Conductivity measurements have verified that it is formed in tetrahydrofuran but not in diethyl ether solution[988–9], a solvent in which B_2H_6 is significantly much less soluble. Evaporation of the tetrahydrofuran solvent leaves only the starting materials, however. Nevertheless the tentative claim has been made, based on inconclusive evidence, that LiB_2H_7 is one of the solids formed from the interaction of triphenylborate with $LiAlH_4$ in ether solution.[239] With KBH_4, $RbBH_4$ and $CsBH_4$ in diglyme the uptake of B_2H_6 is considerably larger than with $NaBH_4$, but the infra-red spectra of the resultant solutions show two kinds of B—H bonds with different frequencies from that pertaining to the BH_4^- ion, and so allow the assumption that the $B_2H_7^-$ anion is initially formed.[990] Instead of B_2H_6, boron trifluoride in calculated amounts can be used to produce the sodium salt in solution, but the product is decomposed by larger quantities.[211]

$$7NaBH_4 + 4BF_3 \xrightarrow{\text{diglyme}} 4NaB_2H_7 + 3NaBF_4$$

$$6NaB_2H_7 + 8BF_3 \xrightarrow{\text{diglyme}} 7B_2H_6 + 6NaBF_4$$

Evidence has been cited against the comparable formation by this method of KB_2H_7 from KBH_4[991, 211], but even here an unexplained delay in the evolution of diborane(6) during the introduction of the BF_3 has been reported.[199] Apart from solubility factors, the reason for the difference in behaviour of sodium and potassium has been explained in terms of the sizes of the cations and a large difference between the lattice energies of KBH_4 and KB_2H_7[437]; an alternative cause could lie in the lower tendency of the potassium ion to become solvated by the diglyme acting as a tridentate ligand, in the manner that has been suggested for Na^+ [727]



The much lower solubility in diglyme of KBH_4 relative to that of $NaBH_4$[211] accords with this suggestion. Yet a further way of producing NaB_2H_7 in solution is the controlled electrolysis of $NaBH_4$ dissolved in diglyme or other polyether: although the heptahydrodiborate(1 –) anion also undergoes electrolysis, in practice this commences only after most of the $NaBH_4$ has been consumed[238, 211]:

$$2BH_4^- \xrightarrow[\text{electrolysis}]{\text{polyether}} B_2H_7^- + \tfrac{1}{2}H_2 + e^-$$

$$B_2H_7^- \xrightarrow[\text{electrolysis}]{\text{polyether}} B_2H_6 + \tfrac{1}{2}H_2 + e^-$$

Solutions of sodium heptahydrodiborate(1 –) in polyethers were found to be better conductors of an electric current than those of $NaBH_4$.[211, 992]

Although NaB_2H_7 is so readily formed in solution in a polyglyme, it has never been isolated free from solvent. If the solvent is evaporated, a solid monosolvate is obtained, and removal of this last molecule of solvent leads to total decomposition[238]: neither could NaB_2H_7 be formed from $NaBH_4$ and B_2H_6 in the absence of a solvent. Apparently the lattice energy of NaB_2H_7 relative to that of $NaBH_4$ is not sufficient for it to have independent existence. Although first attempts to demonstrate the existence of the potassium salt failed[991, 211], infra-red studies are compatible with its formation under comparable conditions[990]: and, more recently, it has been shown that solvates of LiB_2H_7, NaB_2H_7 and KB_2H_7 containing an uncertain number of solvent molecules can also be precipitated at 0°C from diglyme solution by the action of B_2H_6 on the corresponding tetrahydroborates, whereas under like conditions the tetrahydroborates of magnesium, calcium and strontium give solvated forms of $Mg(B_2H_7)_2$, $Ca(BH_4)B_2H_7$ and $Sr(B_2H_7)_2$ respectively.[993] Likewise none of these salts can be freed from the solvent molecules without breaking down completely. But with bulkier cations lattice-energy factors are more favourable, so that both the solvent-free tetrabutylammonium and tetraethylammonium salts, $NBu_4B_2H_7$[436, 994–5] and $NEt_4B_2H_7$[437, 682, 994–5], have been prepared from the solid tetrahydroborates (or tetrahydroaluminates) and B_2H_6. The tetraethylammonium salt is reported to be stable in a dry atmosphere. These salts partly hydrolyze with dilute alkali[994]

$$R_4NB_2H_7 + 3H_2O + OH^- \rightarrow R_4NBH_4 + 3H_2 + B(OH)_4^-$$

are decomposed by amines[994]

$$R_4NB_2H_7 + NR'_3 \rightarrow R_4NBH_4 + H_3B.NR'_3$$

and at 100°C *in vacuo* decompose back to the tetrahydroborate(1 −) and B_2H_6.[994] Such salts have reducing properties and can be used in the direct preparation of alicyclic boranes from cyclic olefins.[996] A comparable salt is the substituted phosphonium analogue $[PMePh_3][B_2H_7]$, which undergoes intramolecular exchange of bridge and terminal hydrogen above 50°C and similarly breaks down at 100°C *in vacuo* to $[PMePh_3]BH_4$ and diborane(6).[985] In an evacuated sealed tube, however, a principal product at 100° is $[PMePh_3][B_3H_8]$.

Other reactions of the $B_2H_7^-$ anion are known. By ^{11}B n.m.r. spectroscopy it has been revealed that $B_2H_7^-$ in diglyme undergoes rapid boron exchange with B_2H_6, but only participates in a slow exchange with BH_4^-, for which the activation energy is *c.* 8·6 kcal mol^{-1}.[50] On storage in polyethers, $B_2H_7^-$ slowly breaks down at room temperature and more rapidly on heating to give the octahydrotriborate(1 −) anion[997–8, 437]

$$2B_2H_7^- \rightarrow B_3H_8^- + BH_4^- + H_2$$

At still higher temperatures polyhedral anions such as $B_{12}H_{12}^{2-}$ and $B_{11}H_{14}^-$ result.[437, 676] Although $B_2H_7^-$ is stated to be stable towards tetrahydrofuran, it is decomposed reversibly by dimethyl sulphide[985]

$$B_2H_7^- + SMe_2 \overset{CH_2Cl_2}{\rightleftharpoons} Me_2S.BH_3 + BH_4^-$$

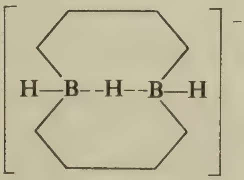
Substituted derivatives of the $B_2H_7^-$ anion are known. These include salts of tetrahydrotrialkylborate(1 −) anions, prepared by the addition of trialkylboranes to tetrahydroborates(1 −) in tetrahydrofuran or polyether solvents[999–1000]

$$BR_3 + MBH_4 \overset{\text{diglyme}}{\rightleftharpoons} M[H_3B{\cdots}H{\cdots}BR_3]$$

Such compounds are hydroborating agents.[1001] Likewise, by using the metal hydride, the hexamethyl substituted salts LiB_2HMe_6 and NaB_2HMe_6 have been prepared

$$2BMe_3 + MH \xrightarrow{\text{diglyme}} M[Me_3B{\cdots}H{\cdots}BMe_3]$$

The infra-red spectra unambiguously establish the singly bridged structure of the anion.[1002] In relation to this, n.m.r. studies have shown that $NaBHEt_3$-BEt_3 mixtures undergo exchange in the presence of ether[982], which suggests the reversible formation of a hexaethylhydrodiborate(1 −) anion. A further interesting $B_2H_7^-$ derivative is the bicyclic bis(1,2-tetramethylene)trihydrodiborate(1–) anion $B_2H_3(C_4H_8)_2^-$ [1003],



prepared as the potassium salt from potassium hydride and bis(1,2-tetramethylene)diborane(6) and readily converted to the tetra-*n*-butylammonium salt.

THE ION $B_2H_8^+$

A positive ion of mass number 30 has been observed in the mass spectra of tetraborane(10) and several higher boranes.[12, 144, 954, 979] If this were entirely due to the species $^{10}B_3^+$ its intensity should not exceed 25% of the intensity of species of mass number 31, but in most cases it is several times as high. There is thus good evidence that the ion $B_2H_8^+$ has been formed, even if at first sight this is somewhat surprising. Its relative abundance in the monoisotopic mass spectra of a number of boranes has been computed.[981] Its detection suggests that BH_4 and BH_4^+ (p. 38) have a definite affinity for each other. The structure of $B_2H_8^+$ is not known, but it presumably contains at least one bridging hydrogen atom.

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SECTION B3

TRIBORANES AND THEIR DERIVATIVES

BY L. H. LONG

INTRODUCTION

Although there are no isolable neutral triboranes, there is good evidence that B_3H_7 and B_3H_9 are capable of transitory existence, and less compelling evidence in the case of other triborane species. In addition, many isolable adducts of B_3H_7 and certain substituted derivatives of B_3H_9 are well characterized and of considerable significance. These are treated in the present section along with a few other compounds.

Of the charged triborane species, the octahydrotriborate(1–) anion $B_3H_8^-$ is of especial importance and is readily isolable in the form of its salts. Charged species encountered as metastable ions in the mass spectrometer are conveniently considered collectively.

METASTABLE TRIBORANE IONS, $B_3H_x^+$ AND $B_3H_x^-$

There being no isolable neutral triborane species, it follows that the metastable positive ions $B_3H_x^+$ are known only from the mass spectra of other boranes such as B_4H_{10}, B_5H_9, and $B_{10}H_{14}$, and of derivatives such as tetraborane(8) carbonyl B_4H_8CO. The whole range of $B_3H_x^+$ ions from $x = 1$ to $x = 9$ has been reported,[1–4] and even that with $x = 10$ from $^{11}B_{10}H_{14}$,[5] though the existence of the last is at first sight surprising. A number of these ions have been produced by secondary processes in work with B_2H_6, partly at higher pressures.[6,7] Several deutero analogues $B_3D_x^+$ have been detected.[8,9] The adduct ion $B_3H_5CO^+$ has been observed.[4]

The negative-ion mass spectra of B_5H_9 and B_4H_{10} have led to the identification of several metastable triborane negative ions $B_3H_x^-$ ($x = 1$–5 and 7).[10,11] Species for which $x = 6$–10 have appeared in the positive-ion bombardment of B_2H_6,[12] where they clearly must arise by secondary processes, but some of them have only been tentatively identified. The ions $B_3H_3^-$, $B_3H_7^-$, and $B_3H_8^-$ have been positively identified in ion-cyclotron studies.[13,14] The structures of several of the known ions have been considered theoretically[176] and topologically,[15] as have those of the unknown doubly charged ions $B_3H_3^{2-}$, $B_3H_5^{2-}$, $B_3H_7^{2-}$, $B_3H_9^{2-}$ and $B_3H_{11}^{2-}$ [15 16]

TRIBORANE(3), B_3H_3

Although adducts of it are known, the free species B_3H_3 has not been reported. There is, however, some evidence that it may have a transitory existence. It is reported elsewhere in this volume (p. 188) that a BH_3 unit can be extracted from pentaborane(9) to give initially B_4H_6. This process can proceed a stage further with the extraction of a second BH_3 unit. With trimethylamine, pentaborane(9) can give the adduct $B_5H_9.2NMe_3$, which on heating *in vacuo* partly dissociates to the starting materials and partly gives $H_3B.NMe_3$ plus a polymeric material of formula $(BH)_x$.[17] This is evidence that some of the B_5H_9 moiety loses $2BH_3$ to leave B_3H_3,

$$B_5H_9.2NMe_3 \xrightarrow{\text{heat}} 2H_3B.NMe_3 + B_3H_3$$

which, being both unsaturated and exceptionally electron deficient, immediately polymerizes, as would be expected and as is also observed in the like case of B_2H_2 (p. 52).

Up to 1·9 molecules of $H_3B.NMe_3$ per molecule of B_5H_9 have been observed.[18] Similar reactions have been noted with dimethylamine $NHMe_2$[19] and methylamine NH_2Me,[20] though competing reactions also occur, while, apparently, these entirely predominate with ammonia. Among the products are reportedly polymerized $Me_2NBH_2.B_3H_3$[19] and $NH_2Me.B_3H_3$,[21] which suggests that B_3H_3 forms adducts and can be fixed with Lewis bases before it polymerizes. Neither B_3H_3 nor its adducts have been produced so far by the use of phosphines, while the much weaker base dimethyl sulphide SMe_2 does not appear to be capable of extracting more than one BH_3 unit from B_5H_9.[22]

B_3H_3 has been given an *ab initio* SCF treatment.[176] The assigned structure is linear, with terminal BH and BH_2 groups.

TRIBORANE(5), B_3H_5

The isolation of gaseous B_3H_5 would not be expected in view of its highly unsaturated nature, which would almost certainly lead to immediate polymerization. However, it has been studied theoretically[176] and assigned a bent chain structure.

There is evidence for an adduct with at least a transitory existence. In studies of the decomposition of tetraborane(8) carbonyl B_4H_8CO, it was concluded that triborane(5) carbonyl B_3H_5CO was initially formed, either by a direct (competing) dissociation, or by the removal of BH_3 in the process[23]

$$B_4H_8 + B_4H_8CO \rightarrow B_5H_{11} + B_3H_5CO$$

Even the adduct of triborane(5) would be expected to condense rapidly, and the product actually observed was a brown CO-containing solid, which however yielded up only very little carbon monoxide on heating *in vacuo*. The molecular-beam mass spectrum of B_4H_8CO has since provided a measure of support for its partial dissociation to B_3H_5CO, since $B_3H_5CO^+$ is observed with a relatively high ion intensity.[4]

There is evidence that B_3H_5 can form stable bis adducts. When B_5H_9 is allowed to react with the phosphine base $PF_2(NMe_2)$, a mixture of products is obtained from which $B_2H_4.2PF_2(NMe_2)$ can be sublimed to leave a solid of lower volatility, that apparently consists essentially of $B_3H_5.2PF_2(NMe_2)$, since on treatment with B_2H_6 it gives equimolecular quantities of $B_4H_8.PF_2(NMe_2)$ and $H_3B.PF_2(NMe_2)$:[24]

$$B_5H_9 + 4PF_2(NMe_2) \rightarrow B_3H_5.2PF_2(NMe_2) + B_2H_4.2PF_2(NMe_2)$$

$$B_3H_5.2PF_2(NMe_2) + B_2H_6 \rightarrow B_4H_8.PF_2(NMe_2) + H_3B.PF_2(NMe_2)$$

In the presence of the cyclopentadienyl anion, cobalt(II) is reduced by NaB_5H_8 in tetrahydrofuran and links up with a B_3H_5 unit in a special kind of bonding to form (among other products) the 6-membered *closo* cage cluster B_3Co_3 in the brown sandwich-type complex $(\eta\text{-}C_5H_5)_3Co_3B_3H_5$,[25] which is stable in air. The cage is a $(2n+2)$-electron system and is essentially octahedral in shape.

A substituted B_3H_5 derivative is the unstable fluorine compound B_3F_5, formed as a minor product when BF_3 is passed over crystalline boron at low pressure and 2000°C.[26] It can be isolated at low temperatures and melts at -55 to -50°C with decomposition. The infrared spectrum of the solid indicates that it has a chain structure with no 3-centre bonds, which is very unlikely to be true of free B_3H_5. It decomposes according to the scheme[27]

$$4B_3F_5 \rightarrow 2B_2F_4 + B_8F_{12}$$

TRIBORANE(7), B_3H_7

Whereas it was at one time thought that B_3H_7 was not capable of existence,[28] the first indication that it occurs as a transitory, non-isolable molecular species was provided by studies of the mechanism of pyrolysis of diborane(6). In order to explain its conversion to tetraborane(10), the earliest investigators found it necessary to propose that B_3H_7 is an essential intermediate,[29] though the mechanism they advanced for its formation is an over-simplification. Independently, other workers[30] observed that the rate-controlling step in the diborane(6) pyrolysis is of order three-halves and has an activation energy of *c.* 27 kcal mol^{-1}. Later workers[31–4] confirmed this and proposed that the rate-controlling step is

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

There is now a wealth of evidence to support this step,[35] and also the conclusion that the reaction is reversible. The same reaction has been invoked to explain the formation of the labelled tetraborane(10) species $^{10}B_3{}^{11}BH_{10}$ from $Na^{10}B_3H_8$, HCl and $^{11}B_2H_6$.[36] The mass-spectroscopic observation of a species with mass number 40 from the interaction of BH_3 with B_2H_6 at 70 mTorr pressure[37] also harmonizes with this, as does the observation of self-exchange of boron in B_2H_6 at 25°C.[38] Isotope-exchange studies carried out with tetraborane(10), in which both hydrogen and boron are observed to exchange, indicate that B_3H_7 is also formed in low concentration by the reversible dissociation[140, 35]

$$B_4H_{10} \rightleftharpoons B_3H_7 + BH_3$$

that occurs as a rate-determining step. There are reasons for believing that this is the initial act in the decomposition of B_4H_{10}.[35] Moreover, the action of atomic oxygen on B_4H_{10} also apparently produces the same triborane species[39]

$$B_4H_{10} + O \rightarrow BH_3O + B_3H_7$$

It is clear also that adducts such as $B_3H_7.OMe_2$[40] or $B_3H_7.OC_4H_8$[41] liberate free B_3H_7 on treatment with the Lewis acid BF_3

$$B_3H_7.L + BF_3 \rightarrow F_3B.L + B_3H_7$$

since other formerly inaccessible triborane(7) adducts such as the carbonyl have been formed by virtue of this reaction, whereas Lewis bases on their own either do not react or do not give the desired products. But the low-pressure thermal decomposition of adducts such as $B_3H_7.PF_2(NMe_2)$

$$B_3H_7.PF_2(NMe_2) \xrightarrow[\text{vacuum chamber}]{\text{heat}} B_3H_7 + PF_2(NMe_2)$$

has been shown mass spectrometrically to constitute the best high-yield source of free molecular B_3H_7.[42] The low-pressure decomposition of $B_3H_7.CO$ is also promising, but this does not appear to have been put to experimental test.

The structure of B_3H_7 has not been determined, although there is little reason to doubt that the three boron atoms will have a triangular arrangement. But unusual difficulties are encountered in trying to decide the positions and bonding of the hydrogen atoms. Early experimental and topological considerations resulted in the favouring of a 2102 structure in the *styx* notation; that is, one containing two BHB bridges, one BBB three-centre bond, no B—B single bonds and two BH_2 groups, and possessing C_s symmetry.[31, 43] But this is merely the least unsatisfactory of a number of structures, none of which is considered satisfactory.[15, 43] In a different topological approach, two structures of higher symmetry were considered.[16] For ready comparison, reference is made to a diagrammatic representation of five conceivable structures.[44] More recently, yet another basic structure has been shown to be favoured by two different theoretical approaches.[45, 46] This has C_{2v} symmetry and is $1103(v=1)$ in the extended *styx* notation.[46] The overall geometry (with the exception of the orientation of one BH_2 group) has been likened to that of the B_3H_7 portion of $B_3H_7.CO$, that is, with a vacant boron orbital replacing the electron pair effecting the bonding with the carbonyl group.[45] This structure is shown schematically in Fig. 1. Two conformers are possible, according to whether the hydrogen atoms attached to the boron atom not involved in hydrogen-bridge bonding are in the plane of the three boron atoms (eclipsed) or in a plane perpendicular to this (staggered). The *ab initio* PRDDO method indicates that the latter

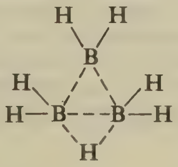


FIG. 1.—Suggested structure (schematic) of B_3H_7 (from Refs. 45 and 46)

conformation is more stable by 8·8 kcal mol^{-1},[46] but a non-empirical MO treatment favours the eclipsed conformation by more than twice this amount (18·1 kcal mol^{-1}).[45] However, another treatment gives the open structure boryldiborane H_2B—B_2H_5.[1006] The B_3H_7 molecule has been described as unsaturated.[46]

Although knowledge of the reactions of B_3H_7 is necessarily limited, a surprising amount can be deduced from indirect evidence. Thus it is known to react reversibly with hydrogen (p. 164), adding on one molecule to form B_3H_9 by a step that has only a low (if any) activation energy, since this step is required to explain the almost quantitative conversion of B_4H_{10} to B_2H_6 by hydrogen.[35] Because B_3H_7 cannot be isolated, it must be presumed to react with itself, even at very low temperatures:

$$\begin{tikzcd} & B_4H_8+B_2H_6 \\ 2B_3H_7 \arrow[ur] \arrow[dr] & \\ & B_6H_{12}+H_2 \end{tikzcd}$$

Thus B_6H_{12} has been detected by mass spectroscopy of decomposing B_4H_{10},[47] and has even been isolated when it is pyrolysed with B_2H_6 in a hot-cold reactor, which condenses out the B_6H_{12} as soon as it is formed.[48] (The function of the B_2H_6, which is thermally much more stable than B_4H_{10}, is to remove the BH_3 produced by the symmetrical dissociation of the tetraborane and so inhibit the back reaction.) The evidence for the alternative production of the non-isolable B_4H_8 by the exchange of a BH unit,[35] if less complete, is still not without strength. At the higher temperatures employed during mass-spectrometric studies with pyrolysing B_2H_6, it was noted that with stepwise increase of the pressure within the reactor triborane, tetraborane, and pentaborane species made their appearances successively,[49, 50] so that conditions could be realized where B_3 but not B_4 fragments were present, whereas at a somewhat higher pressure both B_3 and B_4, but not B_5, fragments appeared. Unless one dismisses this as due entirely to ionic reactions, this can be regarded as evidence that the tetraborane species is formed only after the appearance of a triborane species rather than directly from diborane(6), and then only when the pressure becomes high enough for collisions between the triborane molecules to become important. Further, the spectrum observed for the tetraborane species differed from the well-characterized mass spectrum of B_4H_{10}, the only new tetraborane species likely being B_4H_8. Since $2B_3H_9$ gives $3B_2H_6$, there is a strong suggestion that the species responsible for the production of B_4H_8 is B_3H_7.

The highly reactive species B_3H_7 when in the presence of other boranes can disappear in other ways than by reacting with itself. Indeed, it will react with most boranes, usually by exchanging BH groups, and is to be recognized as an important intermediate in many borane-interconversion reactions.[35] It can also participate in condensation reactions with certain of the higher boranes, and the reaction

$$B_3H_7+B_6H_{10} \rightarrow n\text{-}B_9H_{15}+H_2$$

originally deduced from earlier evidence,[35] has since received direct confirmation.[51] There is no evidence as yet as to whether this reaction proceeds via a metastable intermediate, B_9H_{17}, or by a completely unstable transition complex. In either case, such reactions provide evidence for the formation of three-centre boron bonds from a borane containing an acidic hydrogen atom attached to a boron atom possessing a readily available vacant orbital when it reacts with a second borane containing a two-centre B—B bond. There is evidence that B_3H_7 can participate as an electrophile in organic reactions involving reduction by means of the octahydrotriborate(1−) anion $B_3H_8^-$.[52]

Adducts

Adducts of B_3H_7 are frequently isolable, and—especially when the donor atom is nitrogen or phosphorus—sometimes show a fair stability. They are prepared (*a*) from tetraborane(10) on reaction with a base or a borane(3) adduct of the base, (*b*) from octahydrotriborates, (*c*) by ligand substitution, and (*d*) from free B_3H_7 prepared *in situ*, e.g.:[53–56, 40]

$$B_4H_{10} + 2NMe_3 \rightarrow H_3B.NMe_3 + B_3H_7.NMe_3$$
$$B_4H_{10} + H_3B.L \rightarrow B_3H_7.L + B_2H_6$$
$$NMe_4[B_3H_8] + NHMe_3Cl \rightarrow Me_3N.B_3H_7 + NMe_4Cl + H_2$$
$$B_3H_7.OC_5H_{10} + NMe_3 \rightarrow B_3H_7.NMe_3 + C_5H_{10}O$$
$$B_3H_7 + CO \rightarrow B_3H_7.CO$$

In addition, the electrolytic oxidation of $B_3H_8^-$ at a platinum anode in the presence of a suitable Lewis base leads to the B_3H_7 adduct of the base.[57]

The adducts of B_3H_7 with some simple amines are particularly well defined. The simplest member of the series, the ammonia adduct $H_3N.B_3H_7$, is readily prepared from NaB_3H_8 and NH_4Cl in ether solution.[58] However, other workers claim that the maximum yield from this reaction is only 38 %, whereas the action of ammonia on $Et_2O.B_3H_7$ in ether at -78°C provides yields of up to 94 %.[59] The ammonia adduct is a colourless crystalline solid sublimable *in vacuo* at 40–50°C with a measured enthalpy of sublimation of 17·1 kcal $mole^{-1}$ at 315 K.[59, 60] Its thermodynamic functions over a wide temperature range have been determined.[61] There is an order-disorder transition point at 297·1 K. The dipole moment is 6·5 D.[59] The substance is freely soluble in liquid ammonia, diethyl ether, ethanol, acetone and benzene, but only very slightly so in petroleum ether.[59] The structures of both solid modifications of this exceptionally

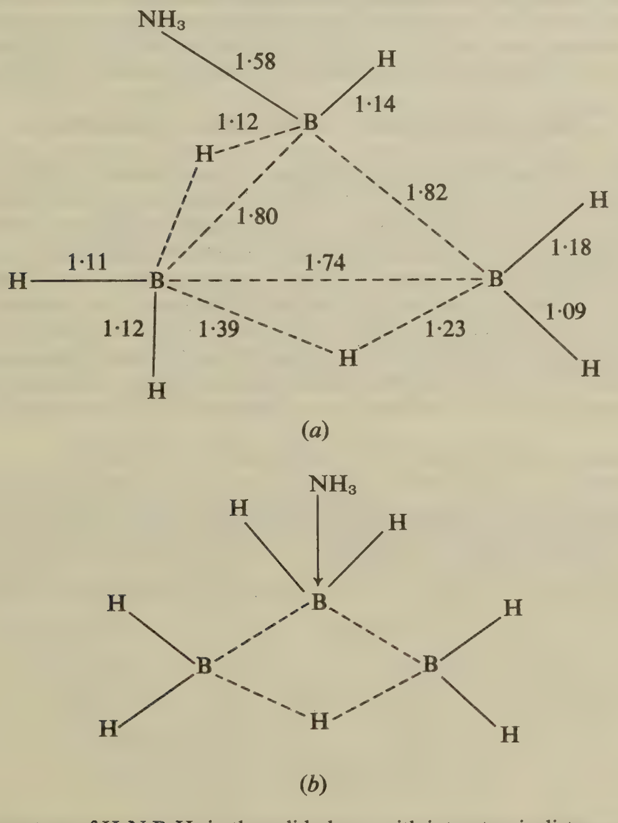


FIG. 2.—(*a*) Structure of $H_3N.B_3H_7$ in the solid phase, with interatomic distances in Ångström units (from Ref. 62). The nitrogen atom does not lie in the BBB plane, but the B—N bond makes an angle of 117·2° with it and angles of 111·0° and 115·3° respectively with the adjacent B—B bonds. (*b*) Idealized symmetrical 1104 *styx* structure

interesting compound have been determined.[59, 62, 63] The molecule has a triangle of boron atoms, the nitrogen being firmly attached to one of these, while the bond between the other two constitutes the shortest of the three B—B distances. The molecular structure in the low-temperature crystalline form is represented schematically in projection in Fig. 2(*a*), in which the nitrogen-boron bond does not lie in the plane of the three boron atoms, but makes an angle of 117·2° with it, and angles of 111·0° and 115·3° respectively with the adjacent boron-boron bonds. This structure is intermediate between 1104 and 2103 in the *styx* notation. The bridge hydrogen atom attached to the boron atom functioning as acceptor is so unequally shared, that the structure is rather close to the idealized 1104 structure of Fig. 2(*b*), which corresponds to the structure of B_2H_6 in which one of the bridge hydrogen atoms has been replaced by a substituted BH_3^- group. To what extent crystal forces are responsible for departure from this idealized structure is not known; but theoretical treatment by three procedures indicates the latter to be the most stable.[64] Although B_3H_7 is a considerably stronger Lewis acid than BH_3, with respect to hydrogen elimination the thermal stability of $H_3N.B_3H_7$ is about the same as that of $H_3N.BH_3$ (p. 19), since the former commences to lose hydrogen at the m.p. of 73–75°C.[58, 59] However, it is remarkably resistant to acid hydrolysis, 6*N* hydrochloric acid requiring several days at 120°C to hydrolyse it completely. It reacts with sodium at −78°C to give $NaBH_4$ and unidentified products.[59]

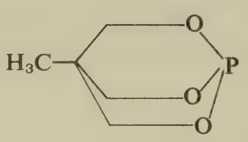
The methylamine and dimethylamine adducts, $H_2MeN.B_3H_7$ and $HMe_2N.B_3H_7$, are prepared in a comparable manner and are very similar to $H_3N.B_3H_7$, but have lower melting points, *c.* 20 and 30°C respectively,[65] whereas the trimethylamine analogue $Me_3N.B_3H_7$ melts at a temperature greater than 200°C. The latter compound, which is also sublimable, was one of the first triborane(7) adducts to be prepared.[53] Unlike the foregoing adducts, it can also be prepared direct from the base by cleavage of B_4H_{10} (*v.s.*)[53, 58] but is itself slowly cleaved further by excess of the base

$$Me_3N.B_3H_7 + 2Me_3N \rightarrow 2Me_3N.BH_3 + \frac{1}{n}\,[BH(NMe_3)]_n$$

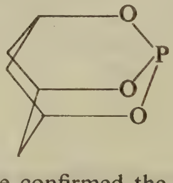
On the other hand, excess B_4H_{10} is catalytically decomposed by $Me_3N.B_3H_7$ to give mainly B_2H_6, B_5H_9 and hydrogen.[53] A better preparation is from the interaction of $NHMe_3Cl$ and NaB_3H_8 in diethyl ether.[31, 55] This adduct manifests a superior stability. It has an order-disorder transition point at 209·6 K, as has been shown in a determination of its thermodynamic functions.[56] The ^{11}B n.m.r. spectrum of $Me_3N.B_3H_7$ dissolved in ether or benzene suggests a structure analogous to that depicted in Fig. 2(*b*), since it shows the superposition of two octets ($J = 35$ Hz), one twice as intense as the other, and is compatible with a model in which two of the boron atoms are equivalent and differ from the third,[66] whereas a rapid base exchange would give equivalence to all of the boron atoms. The field-ion mass spectrum of this compound has been reported.[67]

Pyridine cleaves B_4H_{10} to give $C_5H_5N.B_3H_7$ and $C_5H_5N.BH_3$.[53]

Towards B_3H_7 (as towards BH_3) phosphines frequently show themselves to be the strongest bases, and will displace trimethylamine from $Me_3N.B_3H_7$ or cleave tetraborane(10) to give the phosphine triborane(7). Excess of the base is liable to cleave the product, so that, for example, $B_2H_4.2PPh_3$ is obtained with triphenylphosphine.[68] However, $B_3H_7.PPh_3$ is known,[68] as are the triborane(7) adducts with PMe_3,[69] PHF_2,[70] PF_2NMe_2,[70]



[71] and



[72]

For many of these adducts infrared studies have confirmed the presence of boron-phosphorus bonding, notwithstanding the simultaneous presence of a trivalent nitrogen atom in the case of PF_2NMe_2.[73, 74] Fully halogenated phosphine adducts such as

$F_3P.B_3H_7$ are only formed by the reaction of the phosphine with free B_3H_7 liberated *in situ*.[40] To date, no adducts of B_3H_7 with arsines or stibines have been reported.

There is good reason to believe that B_3H_7 forms non-isolable adducts with elementary oxygen in certain gas-phase reactions. Thus the species B_3H_7O is apparently an intermediate in the oxidation of B_4H_{10}.[75] In addition, it has been necessary to propose the reactions

$$B_3H_7 + O_2 \rightarrow B_3H_7O_2$$
$$B_3H_7 + O_2 \rightarrow B_3H_7O + O$$

to explain the rather complex behaviour of B_2H_6 with oxygen.[76] Of oxygen compounds which do not react destructively with boranes, only ethers have been reported to give adducts of B_3H_7. Though the ether adducts are much less stable than those of amines and phosphines, they are in general readily prepared by the action of the ether on B_4H_{10}.[53] The dimethyl ether complex $Me_2O.B_3H_7$ exerts a vapour pressure of $< 0{\cdot}5$ Torr at its melting point of 11°C, but decomposes at slightly higher temperatures.[77] It is thus considerably more stable than $Me_2O.BH_3$, reflecting the stronger Lewis acid powers of B_3H_7 relative to those of BH_3. The ^{11}B n.m.r. spectrum of $Et_2O.B_3H_7$ in Et_2O shows that all the boron atoms are equivalent, indicating rapid base exchange[78] (contrast $Me_3N.B_3H_7$[66]). In the reaction of tetrahydrofuran C_4H_8O with B_4H_{10}, n.m.r. studies have revealed that the triborane(7) complex is not the first product to be formed by cleavage of the B_4H_{10}, but that the reaction proceeds via the $B_3H_8^-$ ion, which is clearly identifiable at -53°C.[79] The initial cleavage of the B_4H_{10} is thus asymmetric, and is followed by a subsequent reaction involving hydride-ion transfer:

$$B_4H_{10} + 2C_4H_8O \rightarrow H_2B(OC_4H_8)_2^+ + B_3H_8^-$$
$$H_2B(OC_4H_8)_2^+ + B_3H_8^- \rightarrow C_4H_8O.BH_3 + C_4H_8O.B_3H_7$$

The ^{11}B spectrum of $C_4H_8O.B_3H_7$ dissolved in tetrahydrofuran or benzene was at first thought to be compatible with a single octet ($J = 38$ Hz), showing that the three boron atoms (as well as the seven borane hydrogen atoms) are equivalent, which would indicate that, in addition to the type of tautomerism occurring with $Me_3N.B_3H_7$, base exchange is also rapid on the n.m.r. time scale.[66] As mentioned above, this seems to be the case for the diethyl ether adduct. However, for the adduct of the stronger base tetrahydrofuran, by means of improved instrumentation it has recently been demonstrated that there are two kinds of boron atoms (as in the case of the amine adducts), in that two close-lying proton-decoupled peaks with an intensity ratio not far from 2:1 have been resolved.[80] The seven borane hydrogen atoms are nevertheless unquestionably equivalent with respect to the n.m.r. time scale. Substitution reactions with stronger bases are easily realized, e.g.[58]

$$C_4H_8O.B_3H_7 + NH_3 \xrightarrow[-78^\circ C]{Et_2O} H_3N.B_3H_7 + C_4H_8O$$

and such reactions reveal the relative base strengths.

The adducts $Me_2S.B_3H_7$ and $C_4H_4S.B_3H_7$ are likewise formed from the cleavage of B_4H_{10} by dimethyl sulphide and thiophene respectively.[53] The reaction with Me_2S proceeds at -80°C.[81]

The carbonyl of triborane(7) was not known to exist until 1972, since it is not prepared directly from the interaction of carbon monoxide with a borane, nor by a simple base-displacement reaction. Thus B_3H_7CO is much less accessible than B_4H_8CO (p. 190). It is also less stable. The first preparation was realized by base displacement from $Me_2O.B_3H_7$ at low temperature in the presence of the acid BF_3.[40] To explain the known facts, a two-stage reaction must be assumed:

$$Me_2O.B_3H_7 + BF_3 \rightarrow Me_2O.BF_3 + B_3H_7$$
$$B_3H_7 + CO \rightarrow B_3H_7CO$$

The product, B_3H_7CO, is a colourless compound stable only below -30°C. It melts at -93°C and has an extrapolated boiling point of 20·3°C.[41] The crystal structure has been determined, revealing that, otherwise than with $H_3N.B_3H_7$ in the crystalline state, the B_3H_7CO molecule has the *styx* configuration 1104.[41] Its structure has been treated theoretically.[45, 64] On decomposing above $-30°C$ it liberates hydrogen and carbon monoxide and forms a mixture of boranes, but some carbon monoxide is initially retained since other carbonyls are formed and the bis carbonyl $B_2H_4(CO)_2$ (p. 54) is a minor product of decomposition.[82]

It has been claimed that the beryllium dialkyls $BeMe_2$ and $BeEt_2$ interact with tetraborane(10) and mixtures of B_4H_{10} and B_2H_6 to give a number of mobile liquids of low volatility that are B_3H_7 complexes, such as $(BH_2Me)(BeHMe)_4.B_3H_7$ and $BH_3BeH_2(BeHEt).B_3H_7$.[83] By a more complex route, $H_3B(BHMe)_3BeH_2.B_3H_7$ can reportedly be prepared from $(MeBeBH_4)_2$.[84]

Like monoborane(3) BH_3, B_3H_7 can form adducts with charged species. Very little work has been done here, but $B_3H_7CN^-$ has been identified as a major product when sodium cyanide reacts with B_4H_{10} in glyme[85]

$$2B_4H_{10} + 3CN^- \rightarrow 2B_3H_7CN^- + H_3BCNBH_3^-$$

Substituted Derivatives

Little is known about substituted derivatives of B_3H_7. However, a complex of trimethyltriborane(7) $B_3H_4Me_3$ is $(BeHMe)_2(BeH_2)_2(B_3H_4Me_3)_2$, which has been claimed as a product of the interaction of dimethylberyllium with B_4H_{10}.[83] Also the trimethylphosphine adduct $Me_3P.B_3H_6CH_2CH_2BH_2.PMe_3$ has been prepared from the cleavage of 2,4-dimethylenetetraborane (p. 212) by PMe_3.[86]

THE NEGATIVE ION $B_3H_7^{2-}$

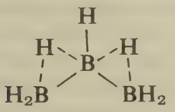
The free negative ion $B_3H_7^{2-}$ is unknown, but it has nevertheless received topological consideration.[15] Neither can the existence of a heptahydrotriborate(2–) anion be claimed, since no salts have been prepared. But metal complexes that formally contain this ion as a π-bonded bidentate ligand have been characterized. Platinum complexes of general formula $(R_3P)_2PtB_3H_7$ have been prepared from *cis*-bis(trialkylphosphine)platinum(II) dihalides by treatment in acetonitrile solution with caesium octahydrotriborate(1–) in the presence of triethylamine[87, 88]

$$cis\text{-}(R_3P)_2PtCl_2 + CsB_3H_8 + NEt_3 \xrightarrow{MeCN} (R_3P)_2PtB_3H_7 + CsCl + NHEt_2Cl$$

where R_3P represents PEt_3, PPh_3, PMe_2Ph, $PEtPh_2$ and tri-*p*-tolylphosphine. Alternatively, such compounds can be prepared from *trans*-$(R_3P)_2Pt(H)Cl$[89]

$$trans\text{-}(R_3P)_2Pt(H)Cl + CsB_3H_8 \rightarrow cis\text{-}(R_3P)_2PtB_3H_7 + CsCl + H_2$$

Even the octahydrotriborate(1–) ion is not essential for the preparation, for in the presence of amine *cis*-$(R_3P)_2PtCl_2$ will react with $(B_2H_6 + BH_4^-)$ to give the same products plus hydrogen.[89] Less well-characterized analogues of palladium and nickel have been prepared,[88] the stability sequence being $Ni < Pd < Pt$. Since the nominal $B_3H_7^{2-}$ ion is isoelectronic with the π-allyl ion, these compounds are sometimes designated π-borallyl complexes. The structure of $(Me_2PhP)_2Pt(\pi\text{-}B_3H_7)$ has been determined by X-ray structure analysis.[88] The B_3 chain is bent (angle = 112·9°), so that each boron atom is within approximate bonding distance of the platinum atom (2·38, 2·18 and 2·13 Å respectively) and the B_3 plane does not contain the Pt atom. Three different PtB_2 planes thus arise, and none of them coincides with the PtP_2 plane. There are no hydrogen atoms bridging the boron to the platinum. Rather, as a first approximation, the two coordination positions on the platinum taken up by the π-borallyl ligand are directed respectively towards one terminal boron atom and the second B—B bond linking the other pair of boron atoms; that is, the ligand is asymmetrically bonded. The bonding at the platinum thus remains strictly planar, even though the angles are distorted from 90°. The heptahydrotriborate(2–) ligand has B—B bond lengths of 1·92 and 1·86 Å respectively and is believed to have the basic structure



(although the hydrogen atoms were not specifically located). There is no bonding between the terminal boron atoms, which are at a distance of 3·15 Å from each other. This structure is generally supported by evidence from the infrared, photoelectron and n.m.r. spectra of the complex, the ^1H n.m.r. spectrum showing that the π-borallyl ligand is stereochemically surprisingly rigid. It is however readily replaced by further phosphine ligands, so that, for example, with PEt_3 $(Et_3P)_2PtB_3H_7$ gives $Pt(PEt_3)_4$.

TRIBORANE(8), B_3H_8, AND THE OCTAHYDROTRIBORATE(1−) ANION, $B_3H_8^-$

Because for isolable boranes of formula B_pH_q the subscripts p and q must either be both odd or both even numbers, there is no likelihood that triborane(8) B_3H_8, which breaks this rule, could ever be isolated. Neither is there evidence that it has been produced as a transitory species. There is however evidence that a transitory addition complex has been detected. In the field ion mass spectrum of $Me_3N.B_3H_7$ (mass number 99), positive ions of mass numbers 100 and 101 have been observed with high intensities.[67] It is thus clear that the species $Me_3N.B_3H_7.H^+$ and $Me_3N.B_3H_7.H_2^+$ must both have transitory existence. It is not known whether the first additional hydrogen atom (proton) attaches itself to the nitrogen atom or the borane moiety, but it is hardly to be supposed that two additional hydrogen atoms are simultaneously linked to the nitrogen atom. It is thus very likely that one of these species is an addition complex of B_3H_8 or $B_3H_8^+$, according to where the positive charge is located.

The stable existence of the octahydrotriborate(1–) anion $B_3H_8^-$ was first demonstrated in 1956 by the isolation of the sodium salt NaB_3H_8. This was originally prepared by the slow reaction of sodium amalgam with diborane(6), which is promoted by ethers[90]

$$2Na + 2B_2H_6 \xrightarrow[25^\circ C]{Et_2O} NaB_3H_8 + NaBH_4$$

The reaction proceeds in a number of steps,[91, 92] which were only partly elucidated. After two days, the NaB_3H_8 is readily separated by virtue of its solubility in ether, and yields of over 80 % have been realized. Sodium amalgam also gives NaB_3H_8, among other products, with pentaborane(11)[93, 94] and with tetraborane(10)[94]

$$2Na + 2B_4H_{10} \rightarrow 2NaB_3H_8 + \tfrac{1}{2}B_2H_6 + \frac{1}{n}(BH)_n$$

Instead of using sodium amalgam, the reaction with B_2H_6 is greatly speeded up by employing the addition compound of an alkali metal with either naphthalene or triphenylborane in tetrahydrofuran solution, when the subsequent addition of NMe_4OH enables the tetramethylammonium salt $NMe_4B_3H_8$ to be readily isolated.[95] The function of the naphthalene or triphenylborane is merely that of an alkali metal carrier. However, attempts to prepare $B_3H_8^-$ salts from B_2H_6 by using the nitrogenous base N,N,2,6-tetramethylaniline to extract a proton from the B_3H_9 believed to be present in B_2H_6 proved fruitless.[31]

Several other ways of preparing octahydrotriborates are known. Ammonia effects ionic or asymmetric cleavage of B_4H_{10}. The stable addition compound $B_4H_{10}.2NH_3$[96] is actually $[BH_2(NH_3)_2]^+[B_3H_8]^-$.[97] Symmetric cleavage of B_4H_{10} is achieved by hydrides and tetrahydroborates, e.g.:[94]

$$NaH + B_4H_{10} \rightarrow NaB_3H_8 + \tfrac{1}{2}B_2H_6$$

$$NaBH_4 + B_4H_{10} \rightarrow NaB_3H_8 + B_2H_6$$

In this way $Mg(B_3H_8)_2$ has been prepared from MgH_2.[98] Other cases of apparently symmetric cleavage of B_4H_{10} to give a B_3H_7 adduct are believed to proceed via an asymmetric cleavage to the $B_3H_8^-$ ion, followed by a hydride-ion transfer.[79] At low enough temperatures, therefore, it may be possible to isolate the ionic compound. Octahydrotriborates have been obtained by the methanolysis of pentaborane(9) in the presence of basic reagents such as tetramethylammonium hydroxide[99] or sodium methoxide:[100]

$$B_5H_9 + 6MeOH + NMe_4OH \xrightarrow[<5°C]{H_2O} Me_4NB_3H_8 + 2B(OMe)_3 + H_2O + 3H_2$$

Likewise the $B_3H_8^-$ ion has been prepared from the degradation of decaborane(14) by methanolysis in the presence of a Lewis base such as diethyl sulphide,[55] in which the crucial step is the methanolysis of the $B_9H_{12}^-$ ion

$$NMe_4B_9H_{12} + 18MeOH \rightarrow NMe_4B_3H_8 + 6B(OMe)_3 + 11H_2$$

However, the $B_3H_8^-$ anion can also be made synthetically, by the action of diborane(6) on a tetrahydroborate dissolved in diglyme at 100°C[95]

$$B_2H_6 + BH_4^- \xrightarrow[100°C]{diglyme} B_3H_8^- + H_2$$

or, as a minor product, from the interaction of pentaborane(9) and $LiBH_4$.[101] Since B_2H_6 can be generated *in situ* by the action of BF_3[102] or iodine[103] on a tetrahydroborate dissolved in diglyme, addition of either to the hot tetrahydroborate solution[95, 104–6] furnishes the octahydrotriborate direct:

$$4BF_3 + 5BH_4^- \xrightarrow[100°C]{diglyme} 2B_3H_8^- + 3BF_4^- + 2H_2$$

$$I_2 + 3BH_4^- \xrightarrow[100°C]{diglyme} B_3H_8^- + 2I^- + 2H_2$$

Indeed, the last reaction provides the most convenient synthesis of octahydrotriborates.

The structure of the $B_3H_8^-$ ion has been shown by X-ray crystal structure determination of $[BH_2(NH_3)_2^+][B_3H_8^-]$[107] to be the symmetrical C_{2v} structure depicted in Fig. 3, being one of the two possible structures predicted by Lipscomb,[43, 108] in

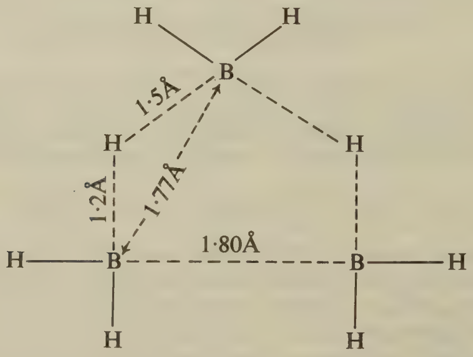


Fig. 3.—Schematic structure of the $B_3H_8^-$ ion, with interatomic distances in Ångström units (from Ref. 107). The ion is not planar, but the three BH_2 groups lie in planes perpendicular to the BBB plane, which is thus a mirror plane. A second mirror plane perpendicular to the first runs vertically through the apexal boron atom

which there are two kinds of boron atoms, situated at the apices of an isosceles triangle. There are three BH_2 groups (2013 structure), and the boron-boron bond distances are intermediate between those found for $H_3N.B_3H_7$ and B_4H_{10} respectively. The terminal B—H bond lengths lie within the range 1·05–1·20 Å. The X-ray pattern has likewise been given for NaB_3H_8,[91] as well as its infrared frequencies in KBr,[91] and those of $NH_4B_3H_8$,[95] which are not inconsistent with the above picture. Presumably the atomic charges on the two types of boron atoms are very similar, because the boron 1*s* core-electron binding energies as determined by X-ray photoelectron spectroscopy with $NMe_4B_3H_8$ are not distinguishable and only a single broad peak is observed.[109] In solution, however, there is no doubt that the boron atoms become equivalent through rapid intramolecular exchange, so that the free $B_3H_8^-$ ion must be regarded as fluxional in character. Not only does the infrared spectrum of NaB_3H_8 become simplified on dissolution in triglyme,[91] but the ^{11}B n.m.r. spectrum of $B_3H_8^-$ in ether, deuterium oxide, or dimethylformamide corresponds with a simple nonet ($J = 32$–33 Hz), in which the two outermost peaks are too weak to be readily observed.[78,55,95] The ^1H resonance is a broad decet.[15] The n.m.r. evidence is only consistent with a model in which all eight hydrogen atoms are also exchanging so rapidly as to appear equivalent on the n.m.r. time scale. For crystalline solids this is also largely true, but the motion of the anion is restricted and transition points have been observed.[110] There is evidence for the presence of ^{11}B-^{10}B coupling in the $B_3H_8^-$ anion.[111]

The free ion has been investigated theoretically by a non-empirical MO approach[112] and also by the FSGO *ab initio* method,[113] which results in a structure of the correct geometry, but bond lengths which are in general considerably longer than the values found experimentally in crystalline salts.

The chemical properties of the octahydrotriborate(1–) anion and its salts have received only a limited study. Some of the salts are comparatively stable. Thus the sodium salt NaB_3H_8 is stable at 200°C, soluble in water, and hydrolyzes more slowly than $NaBH_4$.[114] It forms solvates reversibly with diethyl ether. Solvated molecules of polyethers and certain other donor solvents are held much more tenaciously, *e.g.*, dioxane in the dioxanate $NaB_3H_8.3C_4H_8O_2$.[115,116] This must be regarded as an indication of the acceptor powers of the $B_3H_8^-$ anion. However, the unsolvated salts are easily prepared, and the known salts are too numerous to describe here, but include those of the other alkali metals, thallium(I)[117] and ammonium. The last, $NH_4B_3H_8$, is however very much less stable than its tetraalkylammonium analogues, and its aqueous solutions decompose slowly at 20°C.[117] The salts of methylated polyamines are comparatively stable.[118] Tetrasubstituted phosphonium and arsonium salts are also known. The guanidinium salt $(H_2N)_3CB_3H_8$ has been reported, but is cleaved by hydrazine to BH_4^-, releasing BH_3 and apparently BH, which appears in the form of a polymer.[119] Salts of other less common monovalent cations include $Ph_3SB_3H_8$, $Ph_3SeB_3H_8$, $Ph_4SbB_3H_8$ and $Ph_4BiB_3H_8$ (which is remarkably stable) and also the unstable $Ph_3TeB_3H_8$ and $Ph_2IB_3H_8$.[117] In addition, salts of the divalent cations Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} have been reported.[117] For further information concerning the **salts of the $B_3H_8^-$ anion, see Section B6, p. 354.**

In solution the $B_3H_8^-$ ion is more stable towards base attack than are B_3H_7 adducts. Donors will open the triangle of boron atoms: thus hydrazine N_2H_4 cleaves BH_3 from NaB_3H_8 at room temperature.[98] The hydrogen is sufficiently hydridic for one molecule of H_2 to be cleaved by fairly weak acids, and in this connection the formation of B_3H_7 adducts by $NHMe_3Cl$[55] and NH_4Cl[58] has already been noted (p. 167). With metaphosphoric acid, $NMe_4B_3H_8$ has been observed to give B_4H_{10} in 40 % yield, along with a 4 % yield of B_6H_{12}[120] and traces of B_8H_{18}.[121] It is simple to regard the formation of the hexaborane as resulting from the condensation of two triborane units, while the B_8H_{18} would obviously appear to arise by dimerization of the B_4H_9 radical. Hydrogen chloride plus diborane(6) convert NaB_3H_8 into B_4H_{10}.[36] One of the most interesting condensation reactions of the $B_3H_8^-$ ion is the formation of the icosahedral $B_{12}H_{12}^{2-}$ ion on heating in basic or ethereal solvents,[122,123]

$$5B_3H_8^- \xrightarrow[100°C]{\text{diglyme}} B_{12}H_{12}^{2-} + 3BH_4^- + 8H_2$$

a reaction which has considerable synthetic value. Under certain circumstances, the $B_3H_8^-$ anion will partially hydrogenate a substituted aromatic ring.[124] The oxidation products of the $B_3H_8^-$ anion are not known, but it is not unlikely that B_3H_7 is the first intermediate. At all events electrolytic oxidation at an inert anode in a donor solvent such as acetonitrile or dimethylformamide gives adducts of type $B_3H_7.L$, as does also protonation in acetonitrile.[125] However, electrochemical oxidation in aqueous media leads to the complete destruction of the triborane skeleton.[125]

Complexes Containing the Octahydrotriborate(1−) Ion as a Ligand

In its compounds with the less electropositive metals in Groups II and III, and also with certain transition metals, the $B_3H_8^-$ unit is not present as an ion, but as a ligand that may be either bidentate or tridentate. More stable complexes result when the unit functions as a tridentate ligand,[126] and on occasion a reversible bidentate-tridentate ligand functionality is possible.[126, 127]

A compound in which the $B_3H_8^-$ unit appears as a bidentate ligand is beryllium octahydrotriborate $Be(B_3H_8)_2$, which is readily prepared by metathesis from TlB_3H_8 and $BeCl_2$.[128] It is a volatile liquid, m.p. −51°C, b.p. (extrap.) 108·4°C. The structure of the solid phase has been determined by single-crystal X-ray crystallography.[129] The bonding within the molecule can be represented as shown in Fig. 4, but the molecule has C_2 symmetry and is far from planar, the two BeB_2 planes being perpendicular to one another, so that the bonding at the beryllium atom is distorted tetrahedral. In addition there is folding at each bonded BB axis, the dihedral angle between the planes BBB and BBeB being 115°. Each half of the molecule therefore has a skeleton resembling that of B_4H_{10} (Fig. 2, p. 193) in which a terminal boron atom has been replaced by the shared beryllium atom. The Be—H_μ bond length of 1·504 Å is considerably longer than the average B—H_μ bond length of 1·174 Å, and the HBeH bond angle contained in each half of the molecule is 125·2°. The four other HBeH angles average 102·1°. Other bond lengths and angles are within about 0·05 Å and 4° respectively of the corresponding values in B_4H_{10} (Table II, p. 194). The molecule is highly electron deficient, and the temperature-dependent n.m.r. spectrum of a toluene solution indicates a slight non-equivalence of the two boron atoms linked via hydrogen to the beryllium atom, and also points to fluxional behaviour.[128] Nevertheless, the compound is moderately stable thermally and decomposes only slowly at room temperature, whereas a solution in benzene or toluene can be held for several hours at 80°C. It is however very air-sensitive.

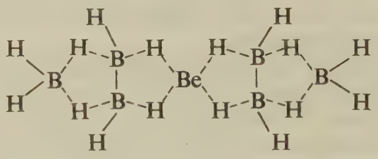


FIG. 4.—Basic structure of $Be(B_3H_8)_2$ (from Ref. 129). The molecular skeleton is far from planar

The volatility of $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$, which are prepared from NaB_3H_8 and Me_2AlCl or Me_2GaCl respectively,[130] suggests that the bonding to the central metal atom is again similar here. These compounds have vapour pressures of 13 and 4 Torr respectively at 0°C. Again their n.m.r. spectra are temperature-dependent, indicating fluxional behaviour. It has been suggested for all of these compounds that by breaking of metal-hydrogen bridge bonds and the forming of new ones, the triborane ligand undergoes what has been termed a *pseudorotation* (which may be over-simplified in the representation in Fig. 5). If this intramolecular exchange is sufficiently rapid, the three boron atoms become equivalent in the n.m.r. spectrum, as do the eight borane hydrogen atoms. This is what is observed at room temperature, but at sufficiently reduced temperatures the boron resonance can be resolved into two signals with relative intensities approximating to 2:1.[130]

Transition metals form similar complexes. The Cu(I) complex bis(triphenylphosphine)copper(I) octahydrotriborate $(Ph_3P)_2CuB_3H_8$, first formed from $(Ph_3P)_2CuCl$ and CsB_3H_8,[131] is a stable crystalline solid of m.p. 158–159°C which is a non-electrolyte

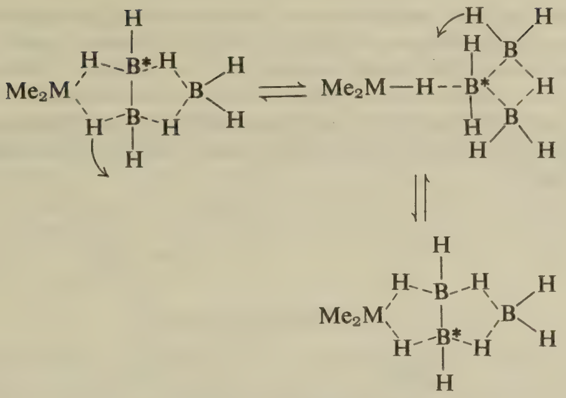


FIG. 5.—Mechanistic representation of pseudorotation of the B_3H_8 group in $Me_2AlB_3H_8$ and $Me_2GaB_3H_8$

when dissolved in acetonitrile. Studies of the crystal structure[132] have shown that the bonding of the metal atom to the borane ligand is precisely comparable with the bonding in the above beryllium, aluminium and gallium compounds. For this compound the rate of intramolecular exchange as a function of the temperature has been calculated from a total n.m.r. line-shape analysis.[133] The comparable, but less stable, complexes $(Ph_3As)_2CuB_3H_8$ and $(Ph_3Sb)_3CuB_3H_8$ have also been described,[134] as has the triphenylphosphite complex $((PhO)_3P)_2CuB_3H_8$,[135] for which n.m.r. studies have shown that the rate of intramolecular exchange is slower than for the triphenylphosphine complex $(Ph_3P)_2CuB_3H_8$. The photosensitive silver compound $(Ph_3P)_2AgB_3H_8$ is preparable, but the corresponding gold compound is reported to be too unstable to isolate.[136] Similar bidentate bonding of the borane ligand to the metal is extant in the volatile dark-blue Ti(III) complex $(C_5H_5)_2TiB_3H_8$, obtained by reducing $(C_5H_5)_2TiCl_2$ with CsB_3H_8.[136] The same is also true for the carbonyl anionic complexes $Cr(CO)_4B_3H_8^-$, $Mo(CO)_4B_3H_8^-$ and $W(CO)_4B_3H_8^-$ obtained by reacting the hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ respectively with the $B_3H_8^-$ anion:[137, 136]

$$Cr(CO)_6 + CsB_3H_8 \xrightarrow[\text{heat}]{\text{polyether}} Cs[Cr(CO)_4B_3H_8] + 2CO$$

A further example is the sublimable neutral Fe(II) compound $(\pi\text{-}C_5H_5)Fe(CO)B_3H_8$, prepared by the ultraviolet irradiation of a solution of $(\pi\text{-}C_5H_5)Fe(CO)_2I$ and $Me_4NB_3H_8$[127]

$$(\pi\text{-}C_5H_5)Fe(CO)_2I + NMe_4B_3H_8 \xrightarrow[\text{U.V.}]{CH_2Cl_2} (\pi\text{-}C_5H_5)Fe(CO)B_3H_8 + NMe_4I + CO$$

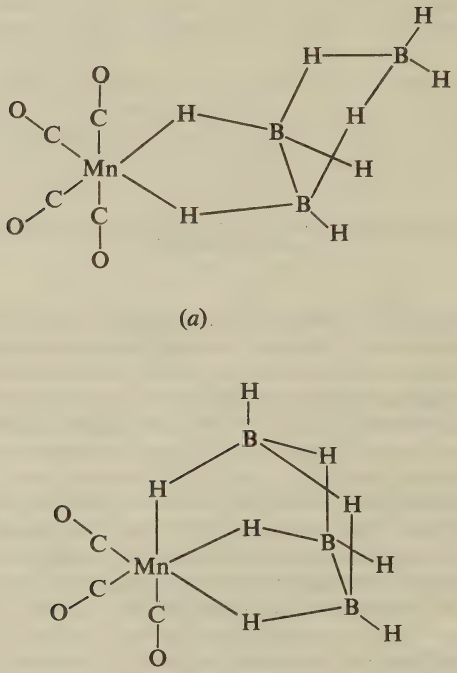
Isoelectronic with the anionic complexes $Cr(CO)_4B_3H_8^-$ and $W(CO)_4B_3H_8^-$ mentioned above are the neutral compounds $Mn(CO)_4B_3H_8$ and $Re(CO)_4B_3H_8$, both of which are volatile liquids prepared by the interaction of $Mn(CO)_5Br$ and $Re(CO)_5Br$ respectively with $NMe_4B_3H_8$ in dichloromethane solution at room temperature for 1–3 days[127]

$$Mn(CO)_5Br + NMe_4B_3H_8 \xrightarrow[25°C,\ 3\ d]{CH_2Cl_2} Mn(CO)_4B_3H_8 + NMe_4Br + CO$$

The manganese complex is yellow, the rhenium colourless. The manganese compound is especially interesting, in that under irradiation with ultraviolet light, either in the vapour phase or in CH_2Cl_2 solution, it loses one molecule of carbon monoxide reversibly, and forms the tricarbonyl compound $Mn(CO)_3B_3H_8$, which is also a yellow liquid and slightly more volatile than the tetracarbonyl complex[127]

$$Mn(CO)_4B_3H_8 \overset{\text{U.V.}}{\rightleftharpoons} Mn(CO)_3B_3H_8 + CO$$

The structures of the two complexes have been elucidated by infrared, and ^1H and ^{11}B n.m.r. spectroscopy. Whereas in $Mn(CO)_4B_3H_8$ the borane ligand is linked to the metal atom in its usual bidentate manner via two bridging hydrogen atoms, in $Mn(CO)_3B_3H_8$ the ligand occupies three of the six co-ordination positions of the manganese and has no BH_2 group. The structural change undergone with the loss of a carbonyl group is accompanied by an increased rigidity of the ligand and can be depicted as in Fig. 6.



(*a*)

(*b*)

FIG. 6.—Structural comparison of (*a*) $Mn(CO)_4B_3H_8$ and (*b*) $Mn(CO)_3B_3H_8$ showing change in the ligand functionality of the $B_3H_8^-$ ligand

The ^1H n.m.r. spectrum consists of two resonances with an area ratio of 3:5, each of which becomes a sharp singlet on decoupling the ^{11}B, showing that the three hydrogen atoms linked to the metal are equivalent, and that the remaining five hydrogen atoms must be undergoing a rapid intramolecular exchange to be equivalent among themselves. The uncoupled ^{11}B spectrum consists of a single very narrow resonance, showing that the three boron atoms are also equivalent. It follows that, precisely as in the case of the free $B_3H_8^-$ ion, the non-bridged boron-boron bond is not in a fixed location, and that its position changes as the three terminal and two boron-bridging hydrogen atoms exchange with one another.[127, 126] This is the first example of a reversible bidentate-tridentate ligand functionality among boranes.

Substituted Derivatives of the Octahydrotriborate(1−) Anion

Until recently, no substituted derivatives of the $B_3H_8^-$ anion had been reported. Most salts of this anion give B_3H_7 adducts when treated with anhydrous HCl or HBr in the presence of a basic ligand such as an ether.[36] However, quite unexpectedly, in diethyl ether or dichloromethane solution the salt of the bulky tetrabutylammonium cation was found to react differently with anhydrous hydrogen halides at reduced temperatures, resulting in salts of the halogenated anions $B_3H_7Cl^-$, $B_3H_7Br^-$ and $B_3H_7I^-$:[138]

$$NBu_4B_3H_8 + HBr \xrightarrow{CH_2Cl_2} NBu_4B_3H_7Br + H_2$$

The salts are crystalline compounds that are moderately stable. The n.m.r. spectra show extreme line broadening and lack of resolution, but the infrared frequencies are consistent with a 2013 *styx* structure. Little is known about their reactions. The strong base triphenylphosphine gives a mixture of products. On heating to 95–100°C, $NBu_4B_3H_8Br$ decomposes in 1·5 h to give pentaborane(9) and diborane(6) as the principal products.[138]

TRIBORANE(9), B_3H_9

Although triborane(9) B_3H_9 has never been isolated, there is much evidence to support the view that the molecular species B_3H_9 is capable of independent existence. Early studies of the kinetics of pyrolysis of diborane(6)[30] led to the conclusion that 'intermediate products' are formed by the interaction of BH_3 with B_2H_6, and later work[31–4] indicated that the first product is B_3H_9

$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9$$

There are reasons for believing that the forward process is exothermic and takes place at almost every collision.[35] The reversibility of the reaction is supported by the kinetics of self-exchange of deuterium in diborane, for which the total reaction order is 1·5,[139–40] as for the pyrolysis of diborane. The evidence is indicative of a low ambient concentration of B_3H_9, and since $[B_3H_9] \propto [B_2H_6]^{1\cdot 5}$ the observed reaction order of 1·5 is readily understood, irrespective of the mode of formation of the B_3H_9. It has belatedly come to be realized[35] that B_3H_9 is also formed directly from diborane(6) in a bimolecular step

$$2B_2H_6 \rightleftharpoons B_3H_9 + BH_3$$

It owes its transitory existence to the fact, that although $2B_3H_9$ is thermodynamically unstable with respect to $3B_2H_6$, B_3H_9 is nevertheless thermodynamically stable with respect to B_2H_6 plus BH_3. It is probably also thermodynamically stable with respect to B_3H_7 plus H_2, and the observation that tetraborane(10) is slowly converted to diborane(6) by hydrogen[141] almost certainly depends on the reaction step[35]

$$B_3H_7 + H_2 \rightleftharpoons B_3H_9$$

It has not been observed in protonation experiments with $B_3H_8^-$.[125] Otherwise no reaction producing B_3H_9 has been proposed, except the initial step in the reaction of NaB_3H_8 with acids[36]

$$NaB_3H_8 + HCl \rightarrow NaCl + B_3H_9$$

The observation of the ions $B_3H_8^+$ and $B_3H_9^+$ in the mass spectrograph[3] might be regarded as further confirmation that B_3H_9 is capable of independent existence.

The only satisfactory structure for B_3H_9 that can be based on the Lipscomb rules is the 3003 structure in the *styx* nomenclature consisting of three BH_2 groups with the boron atoms arranged in an equilateral triangle and joined by symmetrical hydrogen bridges,[142, 43, 46] as depicted in Fig. 7. In common with diborane(6), it consists of BH_2 groups joined by an equal number of hydrogen bonds.

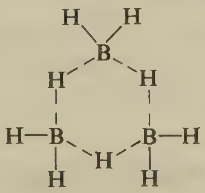


FIG. 7.—Probable structure of B_3H_9 (from Ref. 43). The molecule is not planar, but the three BH_2 groups lie in planes perpendicular to the BBB plane

Refs. p. 182

It is possible to draw certain conclusions about the reactions of B_3H_9. Since it cannot be isolated, even at low temperatures, it must be presumed to react with itself with zero or very low activation energy

$$2B_3H_9 \rightarrow 3B_2H_6$$

In this it is unlike the superficially parallel conversion of the isoelectronic ozone to oxygen, where there is an appreciable energy barrier. Since other modes of decomposition of B_3H_9 are endothermic or associated with large activation energies, the direct conversion to diborane by the foregoing reaction will be essentially responsible for holding down the equilibrium concentration of B_3H_9 in pyrolysing diborane to a very low, but not insignificant, value. As has been seen, other ways in which B_3H_9 can decompose are to $B_2H_6+BH_3$, and to $B_3H_7+H_2$. These are both unimolecular, and the first of these, like the bimolecular decomposition, does not lead to the consumption of diborane. Decomposition to $B_3H_7+H_2$ does do so, however, and appears to be the rate-controlling step in the thermal decomposition of diborane. Its activation energy, first measured in 1951,[29, 30] is *c.* 27 kcal mol^{-1}. That this value is to be associated with the latter mode of decomposition is confirmed by the observation that the reaction order of the rate-controlling step is 1·5 with respect to the diborane concentration;[30] that is, that the rate of diborane pyrolysis is proportional to $[B_2H_6]^{1\cdot 5}$, which in turn is directly proportional to $[B_3H_9]$. The intermediate B_3H_9, like B_3H_7, is thus a vital species in the conversion mechanism of diborane to higher boranes.[31–5]

Other gas-phase reactions for which there is evidence[35] are:

$$B_3H_9+B_3H_7 \rightarrow B_2H_6+B_4H_{10}$$

$$B_3H_9+B_4H_8 \rightarrow B_2H_6+B_5H_{11}$$

$$B_3H_9+B_4H_{10} \rightarrow B_2H_6+B_5H_{11}+H_2$$

$$B_3H_9+B_8H_{12} \rightarrow B_2H_6+n\text{-}B_9H_{15}$$

In all of these reactions the B_3H_9 yields up a BH_3 group. Nothing is known of its reactions with ionic species, but it would generally be expected to react as $B_2H_6+BH_3$.

Adducts

Unlike B_3H_7, B_3H_9 does not form stable adducts at room temperature, and it is uncertain whether it has a weak tendency to form simple coordinate bonds even at reduced temperatures. Diborane(6), to which it is closely related, does form weak bonds of this type with some strong donors (p. 84). Also pyridine borane $C_5H_5N.BH_3$ in diglyme solution adds on B_2H_6 at -64°C to give a product of formula $C_5H_5N.B_3H_9$[143]; but whether the arrangement of the boron atoms is triangular or linear is not yet known, and there is even the possibility that the complex is to be formulated as the ion pair $[C_5H_5N.BH_2]^+[B_2H_7]^-$. A still more uncertain example is the species $Et_2O.B_3H_9$, which has been proposed solely from phase studies of the ether-diborane(6) system at low temperatures.[144] But again there is no evidence regarding the structure, and in this case the observed variation in temperature over the concentration range critical for the correct identification of the phase is so small as to leave room for doubt regarding the experimental evidence and its interpretation in favour of a separate existence for the species. It is also highly questionable whether the peculiar compound nonahydrotriboratoaluminium B_3H_9Al, formed from the pyrolysis of $Al(BH_4)_3$ at 110–40°C[145] with an enthalpy of formation of $14{\cdot}2\pm 1{\cdot}5$ kcal mol^{-1} and stable up to 115°C *in vacuo*, is to be regarded as an adduct of B_3H_9. The compound is hydrolysed by water

$$B_3H_9Al+12H_2O \rightarrow 3H_3BO_3+Al(OH)_3+10\tfrac{1}{2}H_2$$

and forms adducts such as $B_3H_9Al.4NH_3$.

Substituted Derivatives

The number of possible isomers of B_3H_9 substituted at the hydrogen has been calculated.[146, 147] Although no derivatives substituted solely at the terminal positions have been reported, derivatives in which respectively two or three of the bridge hydrogens atoms are substituted by other groups are known. Thus bis(μ-dimethylamino)triborane(9) (Fig. 8) is one of the products of the action of excess diborane(6) on tris-

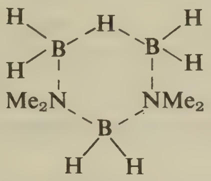


FIG. 8.—Basic structure of bis(μ-dimethylamino)triborane(9) (from Ref. 149)

(dimethylamino)alane in diethyl ether,[148, 149] or, better, on the unstable salt $K[Me_2NBH_2NMe_2BH_3]$, on bis(dimethylamino)borane $BH(NMe_2)_2$ or even on tris(dimethylamino)borane $B(NMe_2)_3$:[149]

$$K[Me_2NBH_2NMe_2BH_3] + B_2H_6 \rightarrow B_3H_7(\mu\text{-}NMe_2)_2 + KBH_4$$
$$BH(NMe_2)_2 + B_2H_6 \rightarrow B_3H_7(\mu\text{-}NMe_2)_2$$

The structure has been confirmed by n.m.r. spectroscopy. The compound $B_3H_7(\mu\text{-}NMe_2)_2$ is volatile, but can be collected in a high-vacuum system at −30°C. It is decomposed thermally at 75°C within 15 min:

$$B_3H_7(\mu\text{-}NMe_2)_2 \xrightarrow[C_6H_5Me]{75^\circ C} B_2H_5(\mu\text{-}NMe_2) + \tfrac{1}{2}(BH_2NMe_2)_2$$

Reactions with diborane(6) and sodium hydride proceed according to the equations:

$$B_3H_7(\mu\text{-}NMe_2)_2 + \tfrac{1}{2}B_2H_6 \xrightarrow[Et_2O]{25^\circ C} 2B_2H_5(\mu\text{-}NMe_2)$$

$$B_3H_7(\mu\text{-}NMe_2)_2 + NaH \xrightarrow[\text{monoglyme}]{} Na[Me_2N(BH_3)_2] + \tfrac{1}{2}(BH_2NMe_2)_2$$

The last reaction is slow. The compound also reacts readily with Lewis bases, though methanol requires the presence of acidic hydrogen:

$$B_3H_7(\mu\text{-}NMe_2)_2 + NMe_3 \rightarrow Me_3NBH_2NMe_2BH_3 + \tfrac{1}{2}(BH_2NMe_2)_2$$
$$B_3H_7(\mu\text{-}NMe_2)_2 + 6MeOH + H^+ \rightarrow 2B(OMe)_3 + [H_2B(NHMe_2)_2]^+ + 5H_2$$

Much more stable and less reactive are the triply bridge-substituted derivatives of B_3H_9. In the known members of this class of compounds, all three bridge hydrogen atoms are replaced by nitrogen, or by other Group-V or Group-VI elements, examples being given in Fig. 9. Such substitution greatly stabilizes the ring and vastly reduces the hydridic character of the terminal hydrogen atoms. The simplest of the nitrogen derivatives, cyclotriboranamine $(BH_2NH_2)_3$, is one of a number of known crystalline cyclic oligomers of boranamine BH_2NH_2 (p. 423) and may be prepared from an alkali metal amide and diborane(6)[150] or its diammoniate,[151] or by the reduction of borazine trihydrochloride:[152]

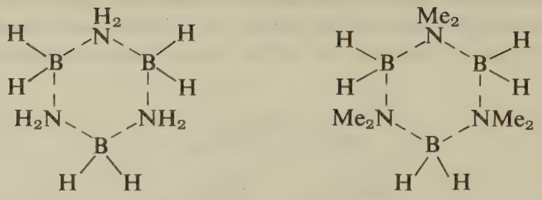
$$LiNH_2 + B_2H_6 \xrightarrow[Et_2O]{} LiBH_4 + \frac{1}{x}(BH_2NH_2)_x$$

$$NaNH_2 + [BH_2(NH_3)_2][BH_4] \xrightarrow[\text{liquid } NH_3]{} NaBH_4 + \frac{1}{x}(BH_2NH_2)_x + 2NH_3$$

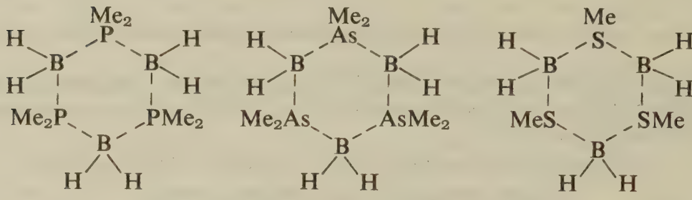
$$2B_3N_3H_6.3HCl + 6NaBH_4 \xrightarrow[\text{diglyme}]{} 2(BH_2NH_2)_3 + 6NaCl + 3B_2H_6$$

It can be sublimed *in vacuo* at 100°C and is soluble in a variety of solvents, including liquid ammonia, ethers, alcohols and water, by which it is not readily attacked. On heating to 150°C or above it decomposes with the loss of hydrogen without melting. The 1,3,5-trimethyl derivative of cyclotriboranamine is very similar and can be prepared by the pyrolysis of methylamine borane[153]

$$3H_3B.NH_2Me \xrightarrow{100^\circ C} (BH_2NHMe)_3 + 3H_2$$



cyclotriboranamine 1,1,3,3,5,5-hexamethylcyclotriboranamine



dimethylphosphinoborane cyclic trimer dimethylarsinoborane cyclic trimer methylthioborane cyclic trimer

FIG. 9.—Examples of μ-substituted derivatives of B_3H_9

and by other methods[154, 155] referred to on p. 424. It commences to lose hydrogen at 180° C and can be separated into two chemically distinguishable isomers by fractional sublimation *in vacuo*.[154] The evidence indicates that the rings have a chair configuration in both isomers and that the isomerism arises through different orientation of the methyl groups, which are all equatorial in the more stable, less volatile isomer, while two are equatorial and one axial in the other isomer. The isomers sublime *in vacuo* at about 70°C and 50°C respectively, and slowly interconvert in liquid ammonia at room temperature. The axial-to-equatorial interconversion of the odd methyl group involves a free-energy change of $-0{\cdot}51$ kcal mol^{-1}. These compounds undergo substitution at the boron by chlorine on treatment with hydrogen chloride. At -78°C reaction occurs with one molecule only:

$$(BH_2NHMe)_3 + HCl \xrightarrow{-78°C} B_3H_5ClN_3H_3Me_3 + H_2$$

At 0°C, however, the more stable isomer reacts with 3 molecules to give the 1,3,5-trimethyl-2,4,6-trichloro compound[156] (Fig. 10), while, probably for steric reasons,

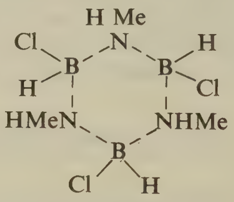


FIG. 10.—1,3,5-Trimethyl-2,4,6-trichlorocyclotriboranamine

the less stable isomer reacts with only 2 molecules to form the 2,4-dichloro substitution product.[156]

The 1,1,3,3,5,5-hexamethyl derivative, $(BH_2NMe_2)_3$, is very different from the foregoing analogues, in that it melts at 97·0–97·8°C, boils at 220°C (extrapolated), is thermally stable to 300°C and is inert towards water and acids at room temperature. It cannot be prepared by comparable methods, all of which give an equilibrium mixture of N,N-dimethylboranamine BH_2NMe_2 and its dimer (p. 425). Though first ascribed the wrong formula, it was discovered by heating BH_2NMe_2 with B_5H_9 or other higher boron hydride, which brings about an irreversible trimerization:[17, 157]

$$3BH_2NMe_2 \xrightarrow[B_5H_9]{\text{heat}} (BH_2NMe_2)_3$$

The precise role of the B_5H_9 is not understood, but it is consumed in proportion to the amount of product formed.[158] The formation of $(BH_2NMe_2)_3$ from BH_2NMe_2 or $(BH_2NMe_2)_2$ appears to be associated with too great an energy barrier for its occurrence in equilibrium studies, and this doubtless enhances the stability of the trimer once it is formed. A non-planar ring in the chair configuration has been demonstrated for this compound by X-ray studies.[159, 160]

The phosphorus analogue, the dimethylphosphinoborane cyclic trimer $(BH_2PMe_2)_3$, is readily formed by pyrolysis of the borane(3) adduct of dimethylphosphine[161]

$$3H_3B.PHMe_2 \xrightarrow{150°C} (BH_2PMe_2)_3+3H_2$$

The very similar dimethylarsinoborane cyclic trimer $(BH_2AsMe_2)_3$ is likewise formed from $H_3B.AsHMe_2$ at 130°C.[162] Such compounds can also be prepared in other ways, as by heating dimethylphosphinyl chloride with sodium tetrahydroborate,[163] or by the thermal decomposition, preferably *in vacuo*, of adducts such as $Me_2NPMe_2.BH_3$ or $Me_2NPMe_2.2BH_3$,[163] $R_3N.BH_2PMe_2.BH_3$,[164] $Me_3N.BH_2AsMe_2.BH_3$,[165] $Me_4P_2.BH_3$ or (better) $Me_4P_2.2BH_3$,[166] and $Me_4As_2.BH_3$:[167]

$$3Me_4As_2.BH_3 \xrightarrow{30\text{–}40°C} (Me_2AsBH_2)_3+3Me_2AsH$$

The trimers are readily separated from smaller quantities of the tetramers and the more highly polymerized amorphous materials that normally accompany their production. The very stable $(BH_2PMe_2)_3$ has m.p. 86°C and b.p. (extrapolated) 235°C, while the only slightly less stable $(BH_2AsMe_2)_3$ has m.p. 50°C and b.p. (extrapolated) 250°C. They are surprisingly inert chemically and require temperatures of 300 and 200°C respectively to effect hydrolysis. The crystal structure of $(BH_2PMe_2)_3$ has been determined.[168] Several analogues and derivatives of these compounds are known, including $(BH_2PEt_2)_3$,[163] $(BH_2PC_4H_8)_3$,[169] $(BH_2P(CF_3)_2)_3$ (m.p. 30·5°C, extrapolated b.p. 177°C),[170] $(BMe_2PMe_2)_3$,[161] $(BMe_2AsMe_2)_3$ (spontaneously inflammable)[167] and $(BMeBrAsMe_2)_3$.[167] No related triborane(9) derivatives containing antimony or bismuth are known.

The sulphur-containing B_3H_9 derivative, methylthioborane cyclic trimer $(BH_2SMe)_3$, was probably one of a series of volatile polymers with the same empirical formula obtained from heating the initial solid product during early studies of the reaction between diborane(6) and methane thiol:[171]

$$MeSH+\tfrac{1}{2}B_2H_6 \rightarrow \frac{1}{n}(BH_2SMe)_n+H_2$$

More recently, Russian workers have shown that the reaction is more conveniently completed in ether solution, and that tetrahydrofuran converts the initial highly polymerized solid product into the trimer, which is a colourless mobile liquid that can be vacuum distilled[172]

$$3(BH_2SMe)_x \xrightarrow{C_4H_8O} x(BH_2SMe)_3$$

Other alkylthio derivatives in the series $(BH_2SR)_3$ have been similarly prepared. They are stable towards air and only very slowly hydrolyzed on heating. The ring structure is less stable than that of the above-mentioned phosphorus derivatives, and is slowly broken up by amines, even in the cold.[173, 174] No analogous selenium- or tellurium-containing derivatives of B_3H_9 have been reported.

THE DECAHYDROTRIBORATE(1−) ANION, $B_3H_{10}^-$

When excess diborane(6) is passed through diglyme in which KBH_4, $RbBH_4$ or $CsBH_4$ is suspended, the solid dissolves; but the uptake of B_2H_6 proceeds well beyond

Refs. p. 182

the point required for the formation of the heptahydrodiborate(1–) MB_2H_7 and continues until the composition in solution is approximately $MBH_4.2BH_3$ or MB_3H_{10}.[175] Like the corresponding MB_2H_7 compounds, these have not been isolated free from solvent and are presumably even less stable, but their existence in diglyme solution is strongly suggested, even if not unequivocally proved. The *styx* structure of the species $B_3H_{10}^-$ has been predicted to be 2005.[15]

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SECTION B4

TETRABORANES AND THEIR DERIVATIVES

BY R. W. JOTHAM AND L. H. LONG

INTRODUCTION

Although tetraborane(10) B_4H_{10} was first definitely prepared as long ago as 1912, it is still the only isolable tetraborane known. It has played a unique role in the history of the boron hydrides, and was in fact the first member of the series to be discovered and characterized by Stock and his co-workers.[1] The achievement was possible only on account of its low rate of hydrolysis: unlike diborane(6), tetraborane(10) is not destroyed under the original preparative conditions, which involve the reaction of magnesium boride with a dilute aqueous acid. But in spite of a greater chemical stability towards water, its thermal stability is low relative to that of diborane(6), and even more markedly so relative to those of pentaborane(9) and decaborane(14). Consequently tetraborane(10) is much less readily available—either in quantity or in a high state of purity—than these other boranes, with the result that it also has a much less extensive literature.

The anions $B_4H_7^-$ and $B_4H_9^-$ have now been characterized, and in addition various other metastable charged species with a transitory existence have been detected. Uncharged fragments are more difficult to detect: tetraborane(8) B_4H_8 is the only one for which definite evidence exists, though derivatives of other hypothetical fragments are known. The above are treated below in order of complexity of the borane species, except that the ions known only in the mass spectrograph are grouped together. Interconversion mechanisms, so far as they are known, are discussed under tetraborane(10).

The original body of this treatise (Mellor, V, 33) gives not only a brief summary of the first papers of Stock, but also a detailed account of earlier pioneer attempts to prepare boron hydrides. In several of these attempts traces of impure tetraborane(10) were probably prepared, but were not fully characterized. Various compilations dealing with the general chemistry of the boranes[2–11] incorporate information on tetraboranes, but only one short review[12] is devoted to tetraborane(10) itself. Other publications[13–25] provide additional data on tetraborane and its derivatives. Mention must also be made of more specialized literature concerning the preparation,[26] structure and bonding,[27–31] chemical reactivity[32–36] and toxicology[37–39] of boranes, as well as that relating to isotopically labelled boron compounds[40] and ^1H and ^{11}B n.m.r. spectra.[41,42] In common with the other boron hydrides, tetraborane(10) is now considered to be too expensive and difficult to handle for use as a rocket fuel,[43,44] but it may have commercial potential as a petrol additive yielding combustion products of much lower toxicity than those from tetraethyllead.[45]

METASTABLE TETRABORANE IONS, $B_4H_x^+$ AND $B_4H_x^-$

All eleven of the $B_4H_x^+$ ions from B_4H^+ to $B_4H_{11}^+$ inclusive have been encountered in the mass spectrometer, and it is convenient to deal with them collectively here. Of these, all except $B_4H_{11}^+$ appear in the molecular-beam mass spectrum of tetraborane(10).[46] In discussing the mass spectrum of diborane(6), it was noted that the parent ion, $B_2H_6^+$, appears only in very low intensity (p. 81). For tetraborane(10) the same is true of its parent ion, $B_4H_{10}^+$, this having an intensity of only about 0·002 of that of the ion $B_4H_6^+$, which is predominant, while the $B_4H_4^+$ and $B_4H_7^+$ ions also show quite high intensities. In the conventional mass spectrum the lighter positively charged tetraborane ions are relatively more intense, possibly because the comparatively long-lived neutral intermediate B_4H_8 appears through decomposition of B_4H_{10} under the prevailing conditions inside the spectrometer.[47] The ionization potentials and (in the absence of experimental evidence) the probable structures of the ions from the fragmentation of B_4H_{10} have been given.[48, 49] The doubly charged ions B_4H^{2+}, $B_4H_3{}^{2+}$, $B_4H_5{}^{2+}$ and $B_4H_7{}^{2+}$ have also been detected in the electron-impact spectrum of B_4H_{10}.[49] The ions $B_4H_4{}^+$ and $B_4H_6{}^+$ are normally also the most abundant tetraborane ions in the mass spectra of higher boranes and their derivatives,[49–56] but the relative abundance of these ions depends markedly on the operating conditions and the preferred decomposition paths. For example, $B_4H_6{}^+$ gives the most intense peak in the molecular-beam mass spectrum of tetraborane(8) carbonyl 1-B_4H_8CO below 75°C, but at higher temperatures $B_4H_4{}^+$ predominates; $B_4H_8{}^+$ is prominent in the mass spectrum of B_5H_{11}, but not in the spectra of B_5H_9 and B_6H_{10}.[57, 49] The heats of formation of $B_4H_4{}^+$, $B_4H_6{}^+$ and $B_4H_8{}^+$ from B_4H_{10}, B_5H_9, B_5H_{11} and B_6H_{10} have been calculated.[49]

The chemical ionization mass spectrum of tetraborane(10) in methane at 140–300 K is of particular interest, in that it shows the presence, not only of $B_4H_7{}^+$ and $B_4H_9{}^+$, but also of the hitherto unknown species $B_4H_{11}{}^+$ in low yield.[58] This apparently arises from the process

$$CH_5{}^+ + B_4H_{10} \xrightarrow{CH_4} CH_4 + B_4H_{11}{}^+$$

in which the function of the excess methane is to remove excess vibrational energy from the $B_4H_{11}{}^+$, which otherwise immediately breaks down into $B_4H_9{}^+ + H_2$. The ion $B_4H_{11}{}^+$ is formed in better yield (moderate intensity) in the chemical ionization mass spectrum of diborane(6) in methane below 140 K or in hydrogen below 115 K,[58] in this case from the reaction

$$B_2H_5{}^+ + B_2H_6 \xrightarrow{CH_4 \text{ or } H_2} B_4H_{11}{}^+$$

The presence of the third body (CH_4 or H_2) is again essential to quench the excess energy of the product. Hexadeuterodiborane(6) will likewise give $B_4D_{11}{}^+$. There is no experimental evidence for the structure of $B_4H_{11}{}^+$, although a possible one has been suggested.[58]

The metastable negative ions from B_4H^- to $B_4H_7{}^-$ have been observed in the negative-ion mass spectra of B_5H_9[56, 59, 60] and B_5H_{11},[56] while $B_4H_7{}^-$, $B_4H_8{}^-$ and $B_4H_9{}^-$ appear in that of B_4H_{10}.[56, 59] Several of these ions and also apparently the ions $B_4H_{10}{}^-$ and $B_4H_{11}{}^-$ have resulted from the positive-ion bombardment of diborane(6) with Kr^+ ions,[61] in which they are formed by secondary processes. Although some of the product ions were positively identified, the identification of $B_4H_{10}{}^-$ and $B_4H_{11}{}^-$ is less certain. The hypothetical ion $B_4H_8{}^{2-}$, which is isoelectronic with B_4H_{10}, has been discussed theoretically.[62] The occurrence of $B_4H_7{}^-$ and $B_4H_9{}^-$ as true anions is treated on pp. 188 and 192.

TETRABORANE(4), B_4H_4, AND THE ION $B_4H_4{}^{2-}$

It has been predicted that, apart from B_4H_{10}, there can be no further tetraboranes based on the icosahedron.[63] Naturally there has been considerable interest expressed in the possible existence of a tetrahedral hydride of formula B_4H_4, but it would presumably be too electron-deficient to exist as a monomer, as are other hypothetical boranes of formula B_nH_n, such as $B_{12}H_{12}$. This reasoning does not apply to the case of the hypothetical anion $B_4H_4{}^{2-}$, since several other hydropolyborate anions of the general formula $B_nH_n{}^{2-}$ (n=6–10, 12) are known and the possible existence of a stable $B_4H_4{}^{2-}$ ion has been predicted on topological grounds.[64] Nevertheless, it is still unknown. The enthalpy of formation of neutral B_4H_4 has been predicted to be 8·3 kcal mol^{-1} from an empirical procedure involving molar enthalpies.[65] LCAO-MO calculations have been undertaken,[66, 67] a minimum basis set of Slater-type orbitals giving the charge on the boron atoms as $-0{\cdot}08$ and the overlap populations in the B—H and B—B bond regions as 0·837 and 0·451 respectively. Other SCF all-electron calculations on both the B_4H_4 molecule and the $B_4H_4^{2-}$ ion have been carried out.[68] In the most recent optimized SCF and LMO studies of B_4H_4, the energy of dissociation into four BH fragments was calculated to be 316·9 kcal mol^{-1}.[69]

A known derivative of B_4H_4 is B_4Cl_4, which is one of the thermal decomposition products of $BHCl_2$.[70] In the vapour phase it is presumably tetrahedral, as its skeletal structure in the crystal is only slightly distorted from that of a regular tetrahedron.[71] The average values for the B—B and B—Cl distances are 1·71 and 1·70 Å respectively. The compound has been partly methylated to B_4MeCl_3 by dimethylzinc, and is converted by dimethylamine into $B_4(NMe_2)_4$.[72]

TETRABORANE(6), B_4H_6, AND THE ION $B_4H_6^{4-}$

Although B_4H_6 would be expected to possess a degree of electron deficiency too great to permit it to appear as a stable monomer, there is evidence that the trimethylamine adduct $Me_3N.B_4H_6$ can be produced in the removal of a BH_3 group from pentaborane(9) by trimethylamine:[73]

$$B_5H_9 + 2Me_3N \rightarrow Me_3N.BH_3 + Me_3N.B_4H_6$$

Nevertheless, it has not been definitely characterized.

The ion $B_4H_6^{4-}$, which is isoelectronic with B_4H_{10}, is not known as a free species; but it may be regarded to exist as a formal ligand in the violet bis(cyclopentadienylcobalt) complex 1,2-$B_4H_6Co_2(\pi\text{-}C_5H_5)_2$ that is isolated as one of the products of reaction of sodium octahydropentaborate(1–) with cobalt chloride and cyclopentadienylsodium[74, 75]

$$NaB_5H_8 \xrightarrow{CoCl_2,\ NaC_5H_5} B_4H_6Co_2(C_5H_5)_2$$

It is doubtless correct to regard the cobalt as formally trivalent, not only on account of the colour and n.m.r. spectrum of the complex, but also because of its relationship with two isomeric complexes of formula $B_4H_8Co(C_5H_5)$ (cf. p. 191), since all three complexes are formally derived from B_4H_{10} by replacing two hydrogen atoms per $Co(C_5H_5)$ group introduced. Two isomeric B-substituted cyclopentyl derivatives of the first complex have also been prepared:[74, 75] these have the formula $c\text{-}C_5H_9B_4H_5\text{-}Co_2(\pi\text{-}C_5H_5)_2$ and are substituted derivatives of the $B_4H_6^{4-}$ ligand.

THE HEPTAHYDROTETRABORATE(1–) ANION, $B_4H_7^-$

In addition to its appearance in the negative-ion mass spectrum of B_4H_{10}, the species $B_4H_7^-$ is known as an anion. The compound which pentaborane(9) initially forms with ammonia at −78°C, $B_5H_9.2NH_3$, may be formulated as a salt of this anion.[76]

$$B_5H_9 + 2NH_3 \xrightarrow[Et_2O]{-78^\circ C} [BH_2(NH_3)_2]^+[B_4H_7]^-$$

There is here an analogy with the compound $[BH_2(NH_3)_2]^+[BH_4]^-$ formed by diborane(6) and ammonia (pp. 86, 111) and with $[BH_2(NH_3)_2]^+[B_3H_8]^-$ formed from tetraborane(10) (p. 172). At low temperatures, trimethylamine[77] and other alkylamines[78] form similar bis adducts with B_5H_9. These products have a very restricted stability, and undergo rearrangement and decomposition on warming: the trimethylamine adduct gives $Me_3N.BH_3$ and other products. A similar pentaborane complex with 2,6-dimethylpyridine has been discussed.[79]

The $B_4H_7^-$ anion is reactive and is converted by ethereal hydrogen chloride into a B_4H_8 complex.[76]

$$[BH_2(NH_3)_2]^+[B_4H_7]^- + HCl + Et_2O \rightarrow [BH_2(NH_3)_2]Cl + B_4H_8.OEt_2$$

Theoretical treatments of the $B_4H_7^-$ anion have been undertaken.[64, 80]

TETRABORANE(8), B_4H_8, AND THE ION $B_4H_8^{2-}$

In spite of the existence of several interesting derivatives of tetraborane(8), free B_4H_8 is not isolable. However, it is an essential intermediate in a number of isotope-exchange and borane-interconversion reactions.[81] There is also convincing indirect evidence that neutral B_4H_8 is formed from B_4H_{10}, B_5H_{11}, some higher boranes, and also from B_4H_8CO, under the conditions of the mass spectrograph.[47,82] Under milder conditions it is formed (no doubt, to some extent, reversibly) from the decomposition of B_5H_{11}[81] and B_4H_8CO[83]

$$B_5H_{11} \rightleftharpoons BH_3 + B_4H_8$$

$$B_4H_8CO \rightleftharpoons CO + B_4H_8$$

but B_4H_{10} preferentially dissociates into $BH_3 + B_3H_7$ rather than $B_4H_8 + H_2$, since at moderate temperatures it exchanges BH_3 with diborane(6) but not H_2 for D_2.[84,85]

The structure of B_4H_8 is not known. Three possible structures have been listed that fit Lipscomb's semi-topological rules,[8] and it has been pointed out[86] that the ability of B_4H_8CO to form labelled molecules on reaction with deuterium or diborane suggests that it dissociates initially to a form of B_4H_8 with yet another structure, in which a vacant orbital is retained.

Several adducts of B_4H_8 are known and some of these are listed in Table I with their physical properties. Presumably B_4H_8 can add directly to ethylene, because C_2H_4 displaces H_2 from B_4H_{10} to give the compound $B_4H_8C_2H_4$.[93,94] This is the bicyclic B_4H_{10} derivative 2,4-(1,2-ethanediyl)-tetraborane(10) or dimethylenetetraborane (p. 211). Other B_4H_8 adducts are produced from pentaborane(11) or by simple displacement. Best known of these is tetraborane(8) carbonyl B_4H_8CO, which, although it has been

Table I.—Physical Properties and References to Spectra of Some Adducts of Tetraborane(8) and Its Derivatives

Compound	Physical property	Reference	References to spectra		
			Infrared	N.m.r.	Mass
1-B_4H_8CO	m.p. −110·3°C	87	87	87, 88	
	b.p. 59·6°C	83			
	vapour pressure, 0°C 71·3 Torr	87			
	vapour-pressure relation: $\log p_{\mathrm{Torr}} = 4{\cdot}555 - 0{\cdot}003\,40T + 1{\cdot}75 \log T - 1649/T$	83			
	Trouton constant 21·0 cal K^{-1} mol^{-1}	83			
1-B_4D_8CO	m.p. −112·2°C	87	87	87, 88	
	vapour pressure, 0°C 74·2 Torr	87			
B_4H_8.TMED[(a)]			89	89	
1-$B_4H_8.PHF_2$	m.p. −80°C	90	90	90	
	b.p. 90·2°C (extrapolated)	90			
	vapour-pressure relation: $\log p_{\mathrm{Torr}} = 7{\cdot}463 - 1667/T$	90			
	Trouton constant 20·98 cal K^{-1} mol^{-1}	90			
1-$B_4H_8.PF_3$	vapour pressure 6·1 Torr at −47·7°C 9·1 Torr at −39·1°C	87, 88	91	91	91
1-$B_4H_8.PF_2X$[(b)]			91	91	91
1-$B_4H_8.PF_2NMe_2$	m.p. −18°C	92		90	
	vapour-pressure relation: $\log p_{\mathrm{Torr}} = 6{\cdot}128 - 1727/T$	92			
$B_4H_4Et_4CO$[(c)]	vapour pressure, 25°C 0·5 Torr	87	87	87	

(a) TMED = N,N,N′,N′-tetramethylethylenediamine.
(b) X = Cl, Br, I.
(c) Alternatively $B_4H_8(C_2H_4)_4CO$. The formulation as $B_4H_4Et_4CO$, though not unlikely, is uncertain.

obtained in a kinetic study of B_4H_{10} at 80–110°C in the presence of carbon monoxide[95, 96]

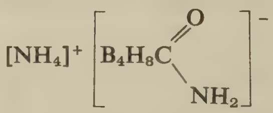
$$B_4H_{10} + CO \rightarrow B_4H_8CO + H_2$$

is better prepared by the reaction of B_5H_{11} with carbon monoxide at room temperature.[83, 88]

$$B_5H_{11} + 2CO \rightarrow B_4H_8CO + BH_3CO$$

A method for preparing B_4H_8CO directly from B_2H_6 and CO is also known.[94] The compound melts at -114°C, has a vapour pressure of 71·3 Torr at 0°C and a boiling point of 60°C. The structure, which harmonizes with Lipscomb's rules,[97] may be considered to be derived from that of B_4H_{10} (p. 193 and Fig. 2) by replacing the two bridging hydrogen atoms linking the boron atom 1 with boron atoms 2 and 4 by a carbonyl group, whereby the lone pair of the carbon atom is accepted by the orbital now vacant on boron atom 1 to form a boron-carbon bond. The compound may thus be more fully designated as 1-B_4H_8CO. This structure is compatible with the 19·3 MHz ^{11}B n.m.r. spectrum of tetraborane(8) carbonyl, in which the resonance for boron atom 1, B(1), is assigned to the doublet at 58·7 ppm ($J_{BH} = 131$ Hz), and the resonances for B(3) and B(2,4) are assigned to the peaks at 2·1 ($J_{BH} = 119$ Hz) and 1·5 ppm ($J_{BH_2} = 127$ Hz) respectively.[86] Liquid- and gas-phase infrared spectra and liquid-phase Raman spectra of 1-B_4H_8CO have been recorded and partly assigned.[98] Molecular-beam mass spectra have also been reported for the compound.[47, 57, 99]

Chemically, tetraborane(8) carbonyl is reactive, but except in the case of substitution it usually does not liberate carbon monoxide when participating in reactions. Thus Lewis bases such as trimethylamine or dimethyl ether produce solid products, but no CO.[83, 88] Hydrolysis produces hydrogen and no carbon monoxide: here hydrogen is apparently lost in the hydrogenation of the CO group, since the amount liberated is considerably less than would otherwise be expected for the B_4H_8 moiety.[88] With ammonia B_4H_8CO forms a bis adduct, which from its reactions is to be formulated[98, 100]



$$[NH_4]^+ \left[B_4H_8C \begin{matrix} \nearrow O \\ \searrow NH_2 \end{matrix} \right]^-$$

and which at low temperatures in liquid ammonia solution is converted by metallic sodium or by sodium tetrahydroborate into the sodium salt $Na[B_4H_8CONH_2]$.[100] Here there is a parallel with borane carbonyl H_3BCO, which gives the salts $NH_4[H_3BCONH_2]$ and $Na[H_3BCONH_2]$.[100, 101] The latter salts may be designated boranocarbamates, since they are formally derived from carbamates by the substitution of an oxygen atom by the isolectronic BH_3 group (p. 17); and apparently a like substitution by a B_4H_8 group is also realizable. The anion $[B_4H_8CONH_2]^-$ is slowly hydrolyzed by aqueous sodium tetraphenylborate $NaBPh_4$ to give the ion $[B_4H_8COOH]^-$[100] analogous to the boranobicarbonate ion $[H_3BCOOH]^-$[102] (p. 17).

Under controlled conditions ethylene adds to tetraborane(8) carbonyl to give $(C_2H_4)_4B_4H_8CO$:[87, 103] its structure is not known, but there is a considerable likelihood that it is to be formulated as $Et_4B_4H_4CO$. At 75°C in a hot-cold reactor, however, ethylene displaces the carbonyl group to give 2,4-(1,2-ethanediyl)tetraborane(10) $B_4H_8C_2H_4$ (p. 211), while other olefins give C-substituted derivatives of this compound[94]

$$B_4H_8CO + \text{olefin} \xrightarrow[\text{hot-cold reactor}]{c.\ 75°C} B_4H_8(\text{olefin}) + CO$$

Other displacement reactions are typified by the reaction of tetraborane(8) carbonyl with hydrogen and with diborane(6), which substitute H_2 and BH_3 respectively for CO:[88]

$$B_4H_8CO + H_2 \rightleftharpoons B_4H_{10} + CO$$

$$B_4H_8CO + \tfrac{1}{2}B_2H_6 \rightleftharpoons B_5H_{11} + CO$$

Deuterium results in the labelled tetraborane μ,1-$B_4H_8D_2$,[86,104] while with boron-labelled diborane, pentaborane(11) is obtained in which the labelled boron atoms are found in both the 2(5) and 3(4) basal positions.[86] The CO group of B_4H_8CO is not satisfactorily displaced by PF_3,[92] but it is smoothly displaced by PHF_2[90] or PF_2NMe_2:[92,98]

$$B_4H_8CO + PHF_2 \xrightarrow{25°C} B_4H_8.PHF_2 + CO$$

$$B_4H_8CO + PF_2NMe_2 \xrightarrow{-20°C} B_4H_8.PF_2NMe_2 + CO$$

The compound $B_4H_8.PF_3$ is however readily formed by the reaction of B_5H_{11} with excess PF_3[87]

$$B_5H_{11} + PF_3 \rightleftharpoons B_4H_8.PF_3 + \tfrac{1}{2}B_2H_6$$

while the complexes $B_4H_8.PF_2X$ [X = Cl, Br, I] are similarly prepared.[91] Because $B_4H_8.PF_3$ is considerably less stable than B_4H_8CO, the PF_3 can be displaced quite readily by CO.[87] The ^{11}B n.m.r. spectra of $B_4H_8PF_3$ are similar to those of B_4H_8CO, except that the high-field B(1) signal becomes a triplet, which has been explained by simultaneous and similar interactions with the attached hydrogen and phosphorus atoms.[86] A preliminary study has been made of the kinetics of thermal decomposition, and an attempt made to explain them is based on the assumption of the formation of an unstable octaborane of formula B_8H_{16} during the second step.[105] The stability of these phosphine complexes suggests that B_4H_8 is a stronger Lewis acid than BH_3.[91]

The analogous difluoro(dimethylamino)phosphine compound $B_4H_8.PF_2NMe_2$ is less readily decomposed and is stable at temperatures up to 55°C.[92] The vapour pressure of the liquid is given by the relationship

$$\log p_{\mathrm{Torr}} = -1727/T + 6{\cdot}128$$

N.m.r. studies indicate that the PF_2NMe_2 ligand is bonded at the phosphorus atom only.[92] X-ray investigations of the solid at -75°C confirm this.[106] The B—P bond distance is 1·856 Å, while the B—B bond distances lie in the range 1·687–1·844 Å. The compound crystallizes in the non-standard monoclinic space group $P2_1/n$, with four molecules in the unit cell of dimensions $a = 11{\cdot}610$, $b = 12{\cdot}046$, $c = 6{\cdot}773$ Å and $\beta = 93°\,32'$. The basic molecular structure is shown in Fig. 1, from which it can be seen that the general structure postulated for such B_4H_8 derivatives receives confirmation. The PNC_2 skeleton of the ligand is essentially planar.

There is evidence that the ether adduct $B_4H_8.OEt_2$ can exist in ethereal solution at low temperatures,[76] since the life of B_4H_8 is prolonged and the solution gives an isolable adduct with the stronger donor Me_2NPF_2

$$B_4H_8.OEt_2 + PF_2NMe_2 \rightarrow B_4H_8.PF_2NMe_2 + Et_2O$$

Another known adduct of B_4H_8 is that with N,N,N′,N′-tetramethylethylenediamine $Me_2NCH_2CH_2NMe_2$ (TMED).[89] It is obtained in high yield when B_5H_9.TMED, formed from B_5H_9 and TMED, is reacted with methanol at 0°C

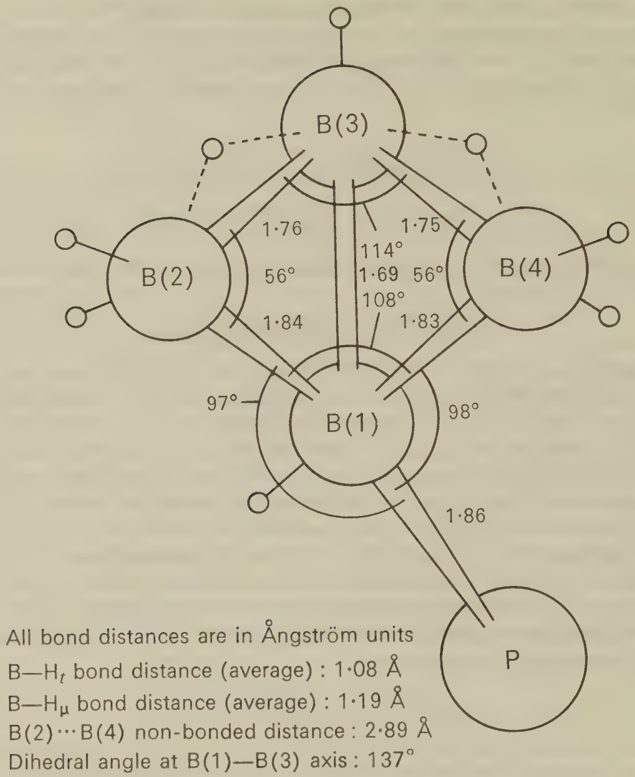
$$B_5H_9.TMED + 3MeOH \rightarrow B_4H_8.TMED + B(OMe)_3 + 2H_2$$

The structure of B_4H_8.TMED is uncertain. Intramolecular dynamic processes both in this complex and in $B_4H_8.PF_2X$ complexes have been discussed.[107]

A substituted derivative of B_4H_8 is $B_4H_6(NMe_2)_2$, which can be isolated as a moderately stable liquid and has been obtained in small yields by heating pentaborane(9) with either dimethylamine or N,N-dimethylboranamine.[77]

The hypothetical ion $B_4H_8^{2-}$, which is isoelectronic with B_4H_{10}, has been discussed theoretically.[62] Formally it occurs as a ligand in the two stable isomeric *nido*-cobaltaboranes of formula $B_4H_8Co(\pi\text{-}C_5H_5)$ that have been reported[74,75] (cf. also p. 188):

$$NaB_5H_8 \xrightarrow[C_4H_8O,\ -196°C]{CoCl_2,\ NaC_5H_5} B_4H_8Co(C_5H_5)$$



All bond distances are in Ångström units

B—H_t bond distance (average) : 1·08 Å

B—H_μ bond distance (average) : 1·19 Å

B(2)···B(4) non-bonded distance : 2·89 Å

Dihedral angle at B(1)—B(3) axis : 137°

FIG. 1.—Basic molecular structure of $B_4H_8.PF_2NMe_2$ with the fluorine atoms and the dimethylamino group omitted. Numbered circles represent boron atoms, small circles hydrogen atoms. The parameters are from Ref. 106 and are rounded to 3 significant figures

THE NONAHYDROTETRABORATE(1−) ANION, $B_4H_9^-$

The $B_4H_9^-$ anion is isoelectronic with tetraborane(10), and the bonding has been discussed in this context.[62] It can be isolated at low temperatures.[108–112] The lithium salt LiB_4H_9 is obtained by the reaction of B_4H_{10} with methyllithium or LiB_3H_8 at −78°C:[108]

$$B_4H_{10} + LiCH_3 \xrightarrow{-78°C} LiB_4H_9 + CH_4$$

Decomposition sets in slowly at −63°C. The compound will give μ-B_4H_9D if treated with DCl, and will deprotonate $B_{10}H_{14}$ but not B_2H_6 or B_5H_9. The implication is that tetraborane(10) is a stronger Lewis acid than diborane or pentaborane(9).[108, 112] It is reported that initially the B_4H_{10} is deprotonated by ammonia in ether at −65°C. On standing, or on raising the temperature, B_4H_{10} and $[BH_2(NH_3)_2][B_3H_8]$ are obtained:

$$2[NH_4][B_4H_9] \rightarrow B_4H_{10} + [BH_2(NH_3)_2][B_3H_8]$$

The more stable tetra-*n*-butylammonium salt of the $B_4H_9^-$ anion is readily obtained by metathesis.[109] Evidence for competing deprotonation and asymmetric cleavage reactions has been obtained from the temperature-dependent ^{11}B n.m.r. spectra of the $B_4H_9^-$ ion, and it has been found that B_4H_{10} is also deprotonated by $(n\text{-Bu})_4NB_5H_8$ or $(n\text{-Bu})_4NB_6H_9$ in dichloromethane and by potassium hydride in ether at −78°C.[109] Dynamic processes within the $B_4H_9^-$ anion have been discussed.[107]

The salt KB_4H_9 reacts with diborane(6) in ether at −35°C to give the salt KB_5H_{12},[113] which in turn liberates B_5H_{11} when treated with anhydrous liquid HCl. The bis adduct which B_5H_{11} forms with ammonia at −112°C has been shown[111] to be the salt $[BH_2(NH_3)_2][B_4H_9]$.

TETRABORANE(10), B_4H_{10}

Molecular Properties and Related Matters

MOLECULAR STRUCTURE

The structures of the boron hydrides have been the subject of important reviews.[30, 114] The molecular structure of B_4H_{10} is shown in Fig. 2. The first study of this structure

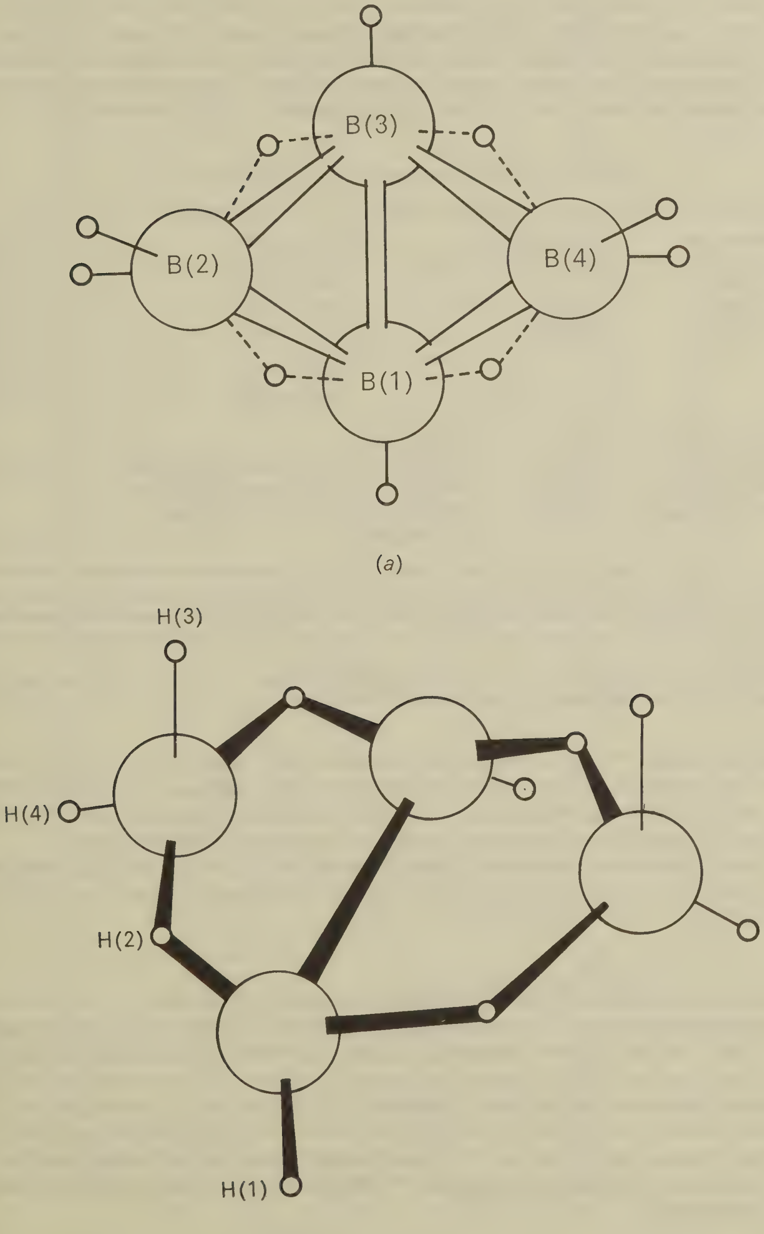


FIG. 2.—Molecular structure of B_4H_{10}. Numbered circles in (*a*) represent boron atoms, small circles hydrogen atoms. For the parameters, see Table II. The lower figure (*b*) further illustrates the geometrical relationship of the four distinct types of hydrogen atoms

was an electron-diffraction investigation in 1938, when an erroneous butane-like structure was suggested; the agreement between the calculated and experimental intensity curves is however strikingly poor.[115] This work was repeated in 1953, when it was found that a structure with a non-planar boron skeleton similar to that depicted in Fig. 2 fits the data much more closely.[116] At this time, a single-crystal X-ray study at low temperature was also carried out.[117, 118] There are four molecules in the monoclinic unit cell, which has $P2_1/n$ symmetry with $a = 8{\cdot}68$, $b = 10{\cdot}14$, $c = 5{\cdot}78$ Å and $\beta = 105° \, 54'$. Later the data were subjected to a least-squares refinement.[119] The molecules occupy general positions in the unit cell such that the individual molecule has a C_1 site symmetry that closely approximates to the C_{2v} symmetry expected for the gaseous state. The data given in Table II are obtained by an appropriate averaging of the refined values.[119] This structure is consistent with those of the other boron hydrides.[30] One interesting feature is that the B(1)—B(3) distance is much the shortest of the various boron-boron distances. This accords with the existence of a true electron-pair bond between these two atoms as required on simple valence theory.[120]

Table II.—Molecular Parameters for Tetraborane(10)(a)

Parameter	Value	Parameter	Value
B(1)—B(3)	1·712 Å	B(1)—H(1)	$1{\cdot}10_5$ Å
B(1)—B(2)	1·842 Å	B(2)—H(3)	$1{\cdot}08_5$ Å
B(2)···B(4)	2·800 Å	B(2)—H(4)	$1{\cdot}10_5$ Å
		B(1)—H(2)	1·16 Å
		B(2)—H(2)	1·37 Å
∠B(1)B(2)B(3)	56° 36′	∠B(3)B(1)H(1)	118°
∠B(1)B(3)B(2)	61° 42′	∠of B(2)—H(3) to plane B(2)B(1)B(3)	122°
∠B(2)B(1)B(4)	98° 00′	∠of B(2)—H(4) to plane B(2)B(1)B(3)	112°
Dihedral angle	118° 06′	∠between planes B(1)B(2)H(2) and B(2)B(1)B(3)	170°(b)

(a) For numbering of the atoms, see Fig. 2. The values for the interatomic distances are the averaged least-square refinements taken from Ref. 119 and have standard deviations of 0·005 Å for B—B distances and 0·03 Å for B—H distances. The angles are taken uncorrected from Ref. 117.

(b) With respect to the internal or 'concave' side of the plane of the boron atoms (see Fig. 2), i.e., the bridge hydrogen atom is slightly above this plane.

For such a structure a non-zero dipole moment would be expected. As measured in benzene solution by the heterodyne-beat method, the dipole moment is $0{\cdot}56 \pm 0{\cdot}01$ D at 25°C.[121]

VIBRATIONAL SPECTRA

Vibrational spectroscopy has been applied to various problems in boron chemistry[122] and to the determination of individual boron hydrides in mixtures.[123] Use of the peak at 2150 cm^{-1} in the infrared spectrum of B_4H_{10} has been recommended for analytical work. The spectrum of B_4H_{10} over the range 670–5000 cm^{-1} is reproduced in Fig. 3.

Detailed studies of the infrared spectra of B_4H_{10} and B_4D_{10} in the gas and solid phases have been carried out.[124–7] Raman frequencies have been measured in the liquid and solid phases, and 31 of the 36 fundamental vibrations and some overtone and combination bands tentatively assigned.[126] The infrared spectrum of μ-B_4H_9D has also been published.[128]

ULTRAVIOLET SPECTRUM

Stock reported otherwise unpublished work on the ultraviolet absorption spectrum of B_4H_{10},[2] which shows many similarities to the spectrum of butadiene.

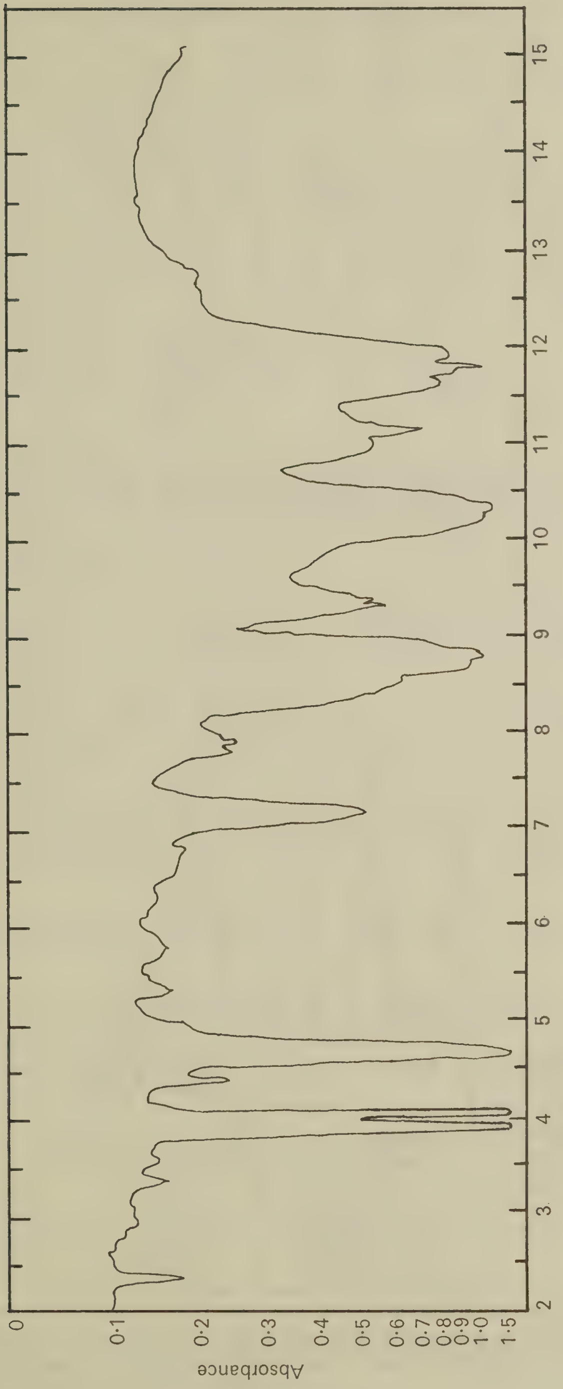


FIG. 3.—Infrared absorption spectrum of B_4H_{10} at 28°C and 102·7 Torr after Ref. 123

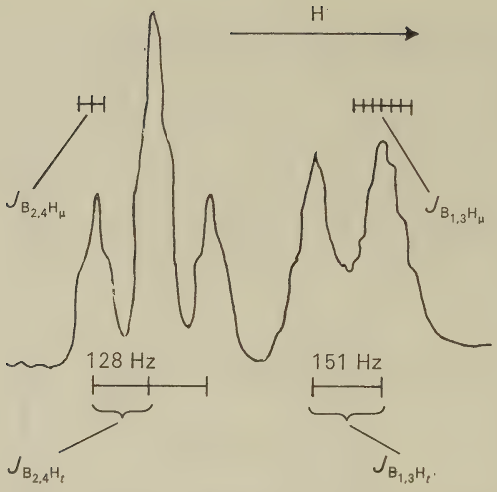


FIG. 4.—12·8 MHz ^{11}B n.m.r. spectrum of B_4H_{10} after Ref. 130, but with the intrepretation corrected according to Ref. 131

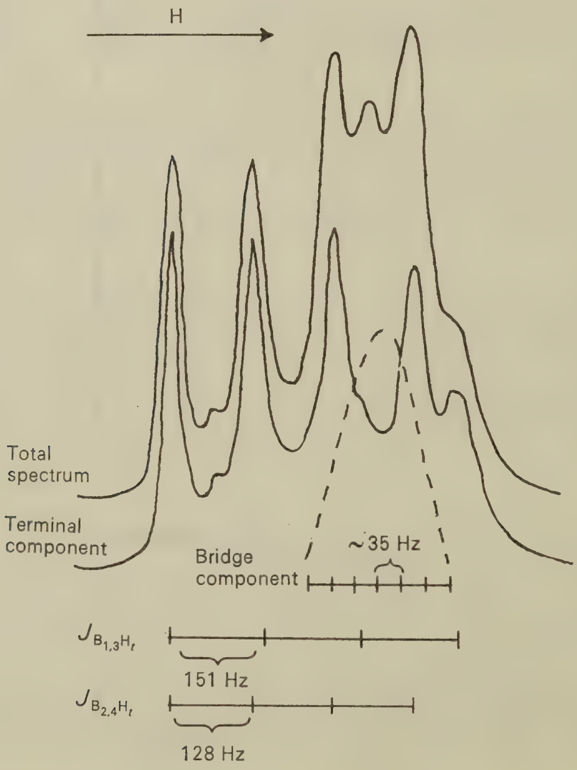


FIG. 5.—40 MHz ^{1}H n.m.r. spectrum of B_4H_{10} after Ref. 130

NUCLEAR MAGNETIC RESONANCE SPECTRA

The n.m.r. spectroscopy of boron compounds has been discussed,[41] while an account of the use of n.m.r. techniques in the analytical study of compounds of carbon, boron and hydrogen has been given.[129] No less than eleven spectra of isotopic tetraboranes under different conditions of resolution are given in the book by Eaton and Lipscomb.[42] In Fig. 4 the 12·8 MHz ^{11}B spectrum and in Fig. 5 the 40 MHz ^{1}H spectrum of the isotopically normal species are reproduced.

A preliminary report of the ^{11}B spectrum was given as early as 1954,[132] while details of another spectrum of low resolution appeared later.[133] Latterly the ^{11}B and ^{1}H n.m.r. spectra of B_4H_{10} and its isotopically substituted homologues have been studied in great detail, largely as a result of an early suggestion that the fine structure of the boron spectrum resulted from ^{10}B-^{11}B coupling.[130] This hypothesis was subsequently shown to be incorrect when it was found that the fine structure arises from a complex interaction with both terminal and bridge protons.[131, 134, 135] Nevertheless, a very weak ^{10}B-^{11}B coupling was eventually detected.[131, 136]

The BH_2-group nuclei resonate at a lower applied field than those of the BH groups, both in the ^{11}B and the ^{1}H spectra; the bridge hydrogen atoms resonate at highest fields in the ^{1}H spectra. One group of workers placed the ^{11}B BH_2 triplet resonance at 6·9 ppm ($BF_3.OEt_2=0{\cdot}0$) with $J_{BH}=132$ Hz, and the BH doublet resonance at 40·8 ppm with $J_{BH}=156$ Hz,[137] whereas another group gave 128 and 151 Hz respectively and reported that the BH doublet shows a septet fine structure for each component, which they ascribed either to ^{10}B-^{11}B coupling or, less probably, to coupling with the bridge protons.[130] Several combinations of ^{10}B-, ^{11}B- and D-isotope enrichment and double irradiation have been used to check on the origin of the fine structure of the ^{11}B doublet.[131] This work shows that the fine structure in fact arises mainly from coupling to the bridge protons,[131] but that the loss of resolution with increasing ^{10}B concentration is due to weak coupling of ^{10}B with the ^{11}B-^{1}H spin-coupled systems.[136] The 220 MHz ^{1}H spectra of B_4H_{10} and of the isotopic species $^{10}B_4H_{10}$ and $^{11}B_4H_{10}$ have been obtained, although details are quoted only for the normal species; the 70·6 MHz ^{11}B spectrum of B_4H_{10} is also recorded, along with the results of multiplet-decoupling experiments at 100 MHz.[138, 139] In this work the two magnetically non-equivalent sets of protons belonging to the BH_2 groups are distinguished for the first time. Relevant parameters are listed in Table III. These are probably the most precise n.m.r. data so far available for this compound. High-resolution spectra obtained by a triple-resonance method indicate an upper limit of 0·3 Hz for B-B coupling constants.[140]

The n.m.r. spectra of μ-B_4H_9D[128] and μ,1-$B_4H_8D_2$[86] have been recorded.

Table III.—N.m.r. Data for Tetraborane(10)(a)

Nucleus(b)	Chemical shift (ppm)	Coupled nuclei(b)	Coupling constant (Hz)	
			From ^{1}H resonance	From ^{11}B resonance
H(1)	8·66(c)	B(1)-H(1)	155	160
H(3 or 4)	7·74(c)	B(2)-H(3 or 4)	134	132
H(4 or 3)	7·54(c)	B(2)-H(4 or 3)	125	
H(2) ($=H_\mu$)	11·38(c)	B(1)-H(2)	>35	~ 23
B(1)	41·8(d)	B(2)-H(2)	<30	~ 30
B(2)	5·16(d)	B(1)-B(2)		$<0{\cdot}3$

(a) Data taken from the 220 MHz ^{1}H and 70·6 MHz ^{11}B spectra of Ref. 139, except that the figure for the B(1)-B(2) coupling constant is from the high-resolution triple-resonance spectrum of Ref. 140.

(b) For numbering of the atoms, see Fig. 2.

(c) Relative to tetramethylsilane = 10·00 ppm.

(d) Relative to $BF_3.OEt_2=0{\cdot}00$ ppm.

MASS SPECTRA

The application of mass spectrometry to the study of the boron hydrides has been discussed.[50] The ions $B_4H_6^+$ and $B_4H_4^+$ are the dominant $B_4H_x^+$ species in the ordinary mass spectrum of tetraborane(10). The most recent data[141] are tabulated in Table IV.

Table IV.—Observed Intensities in the Monoisotopic Mass Spectrum of Tetraborane(10)[(a)]

Ion	Relative intensity	Ion	Relative intensity	Ion	Relative intensity
$B_4H_{10}^+$	0·02	$B_3H_6^+$	2·31	$B_2H_6^+$	0·10
$B_4H_9^+$	0·39	$B_3H_5^+$	14·0	$B_2H_5^+$	2·31
$B_4H_8^+$	8·22	$B_3H_4^+$	6·37	$B_2H_4^+$	0·74
$B_4H_7^+$	13·0	$B_3H_3^+$	11·7	$B_2H_3^+$	1·99
$B_4H_6^+$	100·0	$B_3H_2^+$	10·5	$B_2H_2^+$	3·07
$B_4H_5^+$	13·4	B_3H^+	2·49	B_2H^+	0·32
$B_4H_4^+$	58·5	B_3^+	1·30	B_2^+	(omitted)
$B_4H_3^+$	18·6			BH_3^+	0·60
$B_4H_2^+$	15·4			BH_2^+	7·04
B_4H^+	10·5			BH^+	1·72
B_4^+	5·26			B^+	9·14

[(a)] Values taken from Ref. 141. The root-mean-square deviation is 0·03.

The ion ratio $B_4H_{10}^{2+}:B_4H_{10}^+$ in the mass spectrometer has been measured as 0·0009.[142] An electron-impact study of the fragmentation of tetraborane(10) has also been carried out.[48] From mass-spectral data on the isotopic species $^{11}B_4H_{10}$, $^{11}B_4D_{10}$ and $B_4H_8D_2$ and from metastable transitions in the first two, it was found that the decomposition paths showed successive losses of two hydrogen atoms from $B_4H_{10}^+$ to B_4^+ and from $B_4H_9^+$ to B_4H^+, as well as the specific transitions $B_4H_{10}^+ \rightarrow B_4H_9^+$, $B_4H_8^+ \rightarrow B_4H_5^+$ and $B_4H_7^+ \rightarrow B_4H_4^+$. Activation energies for the transition states are 2 eV or less.[48] In a later paper the ionization potentials of B_4H_{10} and B_4D_{10} were given as $10{\cdot}4 \pm 0{\cdot}1$ and $9{\cdot}9 \pm 0{\cdot}1$ eV respectively.[49] A mass-spectral investigation of the pyrolysis of tetraborane(10) has been carried out.[143] A further mass-spectral analysis of the isotopically labelled tetraboranes $^{10}B_4H_{10}$, $^{10}B_4D_{10}$, $^{11}B^{10}B_3H_{10}$ and μ-$^{10}B_4H_9D$ showed that the $B_3H_x^+$, $B_2H_y^+$ and BH_z^+ fragments are formed by non-random dissociation of the $B_4H_w^+$ frameworks.[46]

An important advance in the interpretation of the mass spectrum of tetraborane(10) has been made by Stafford *et al.*[47] These workers have performed molecular-beam experiments that greatly reduce the pyrolysis of unstable species in the mass spectrometer. In this way it was possible to obtain spectra of B_4H_{10} and B_4H_8CO that were not complicated by ions from B_4H_8, which was thereby shown to be a comparatively long-lived tetraborane at relatively high temperatures.[57] An analysis of the normal mass-spectrum of B_4H_{10} is reproduced in Fig. 6. Stafford goes as far as to state that 'previous appearance potential and theoretical fragmentation studies of B_4H_{10} are virtually meaningless.'[82] It is however important to note that, as discussed on p. 220, B_4H_{10} does not decompose significantly into $B_4H_8 + H_2$ by a single homogeneous process at moderate temperatures.

The field-ion mass spectrum of tetraborane(10) has been studied.[365]

Although the ion $B_4H_8^+$ normally predominates, $B_4H_9^+$ is the dominant ion in the mass spectrum of CH_4-B_4H_{10} mixtures at 80°C,[144] a fact that is to be attributed to ionization by a chemical process. Ion-molecule reactions of B_4H_{10} have also been studied by ion-cyclotron resonance.[145] The ion $B_4H_{11}^+$ can be formed in this system at a lower temperature; however, as discussed on p. 187, a study of the systems B_2H_6-CH_4 and B_2H_6-H_2 has disclosed that $B_4H_{11}^+$ can be formed in higher yield by a different ion-molecule reaction at low temperatures.[58] This study has revealed that the proton affinity of B_4H_{10} has the value 144 ± 5 kcal mol^{-1}.

The negative-ion mass spectrum of tetraborane(10) when bombarded by electrons

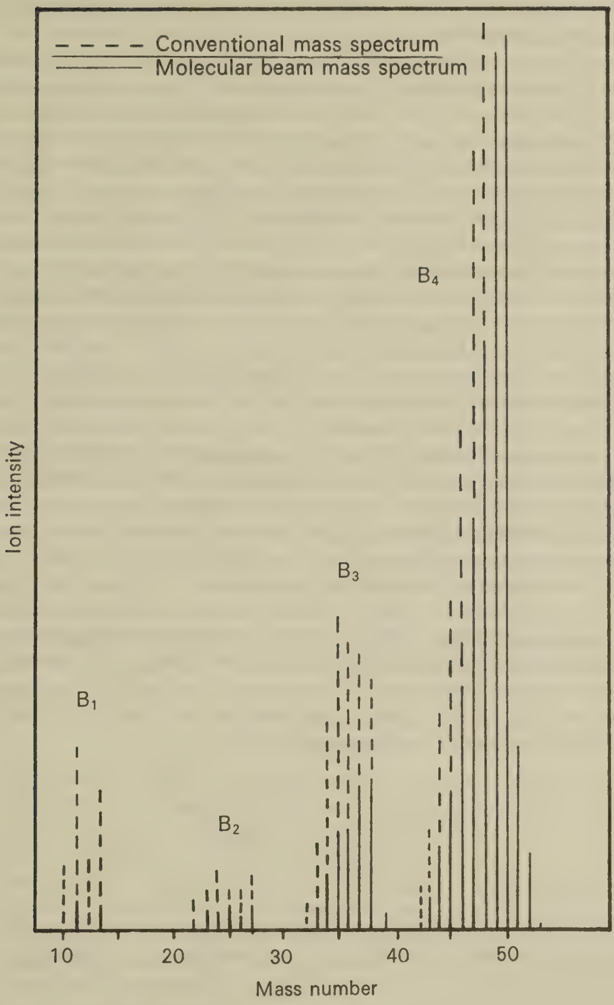


FIG. 6.—Comparison of the conventional and molecular-beam mass spectra of B_4H_{10} after Ref. 46. The difference has been attributed to decomposition to B_4H_8 and other species in the conventional ion source—but see also Ref. 82

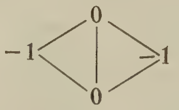
has also been studied.[59] In addition to the production in low intensity of a few $B_4H_x^-$ ions, as mentioned previously (p. 186), together with some $B_2H_x^-$ and BH_x^- ions, the $B_3H_7^-$ ion is produced in strikingly high intensity,[59,145] which suggests the ready elimination of a neutral BH_3 group during electron bombardment.

THEORETICAL STUDIES

A long list of early papers in which investigators had speculated upon the structures of the boron hydrides is cited by Stock,[2] and the problems which the structure and bonding of these compounds raised at earlier stages in the development of knowledge concerning them have been discussed by others.[27,28] The clarification of this complicated set of problems was largely due to Lipscomb, and the key conceptual advances are summarized in his book.[8] Other workers, who have followed these ideas, have now developed methods of constructing models of the higher boranes that are comparable with those used in the teaching of organic chemistry.[146]

A preliminary discussion of the valence structures of the boron hydrides was given in 1954.[120] In tetraborane(10) the boron atoms numbered 2 and 4 (Fig. 2) form two B—H single bonds and two B - - H - - B three-centre bonds, namely one to each of boron atoms 1 and 3. Formal account is thus taken of all the valence electrons of boron atoms 2 and 4. Boron atoms 1 and 3 form only one B—H single bond so that, in order to bring their electronic structures to that of an octet, a B(1)—B(3) single bond of conventional type is required to complete the formal valence description of the compound.[120] The existence of this B—B single bond finds support in many theoretical studies, most recently in the results of a theoretical treatment based on accurate self-consistent-field wave functions and involving maximization of the coulomb repulsions of electron pairs within orbitals, which treatment also indicates that most of the delocalization is associated with the two boron atoms of the BH_2 groups.[31]

In a series of papers, Lipscomb had meanwhile developed semitopological rules relating valence theory and bonding in the boron hydrides.[29, 64, 97, 147] For these rules, any boron hydride is described by the topological label ($s\ t\ y\ x$), where s is the number of bridging hydrogen atoms, t is the number of B_3 three-centre bonds, y is the number of B—B single bonds and x is the number of BH_2 groups. Thus the structure of tetraborane(10) is represented as (4 0 1 2), i.e., as one requiring no B_3 three-centre bonds. Simple relationships between s, t, y and x are readily obtained, from which it is evident that another possibility for a hydride of formula B_4H_{10} is one with a (3 1 0 3) structure. An icosahedral fragment of this type has a very unsatisfactory structure,[8] but this is not the only possibility, since the boron skeleton of such a hypothetical hydride could be a trigonal pyramid of symmetry C_{3v}: three BH_2 groups of this structure define an equilateral triangular base, which is held together by the three-centre bond; the apical BH group is bonded to each of the basal boron atoms by a bridging hydrogen atom. The actual C_{2v} structure of B_4H_{10}, on the other hand, gives rise to a unique bonding description. Conversely, the (4 0 1 2) valence structure is sufficient to establish a unique spatial structure, as may be seen from the following excess-connectivity diagram of tetraborane(10):[8]



Tetraborane(10) is the smallest boron hydride which is clearly seen to be an icosahedral fragment (diborane(6) admittedly corresponds to a single edge of an icosahedron). The tendency towards the icosahedral ordering of the boron skeleton of boranes can be understood as arising from the electron deficiency with consequent triangulation of groups of three adjacent boron atoms. Three equivalent orbitals centred at the corners of a triangle give rise to one strongly bonding combination (a three-centre orbital) and two antibonding orbitals, which are degenerate if the triangle is equilateral. The electron deficiency of the system is accommodated by this 'one-bonding-molecular-orbital-from-three-atomic-orbitals' arrangement; the hydrogen bridges provide a similar arrangement for the electrons used in bonding at a peripheral edge. These guiding principles can be readily correlated with the B_4H_{10} structure (Fig. 2). Lipscomb has shown that there can be no other tetraborane which is based on the icosahedron.[63]

Simple LCAO-MO calculations have been carried out for B_4H_{10} and other tetraboranes.[66, 148] With tetraborane(10) the results were very sensitive to the model chosen: for example, although the charge density on the boron atoms was always found to be small, the different models did not decide which boron atoms were the more electronegative. A self-consistent-field calculation on B_4H_{10}, using linear combinations of Slater-type orbitals, gave the charge distribution (which again turned out to be ambiguous), the bond overlap populations, the bond and dipole moments and the total energy of the molecule.[149] The total bond energy was calculated to be 1122 kcal mol^{-1}, to be compared with the experimental value 1058·95 kcal mol^{-1} (see p. 201). A summary of these developments has been given,[8,150] since when more precise SCF calculations on tetraborane(10) and the pentaboranes have been presented.[151] These calculations suggest that all atomic (Mulliken) charges are less than ±0·1: apical boron atoms are more electronegative than other boron atoms, boron atoms in BH_2 groups are more electropositive than those in BH groups, while no simple correlation exists between the one-centre diagonal F-matrix elements and the charge. Further, it is indicated that all terminal hydrogen atoms are negative and all bridge hydrogen atoms positive, and that hydrogen atoms bridging BH and BH_2 groups are more strongly bonded toward the BH group (Fig. 2), while a very low electron density directly between two boron atoms is indicated when these are joined by a hydrogen bridge. In Fig. 2 the stronger B—B bonding between the unbridged boron atoms 1 and 3 is clear from the much shorter bond length. The molecular-momentum distribution and the Compton profile of tetraborane(10) have been calculated from the analytical functions thus obtained.[151,152]

Non-orthogonal orbitals localized in the bond regions are readily constructed from a diffuse but orthogonal set of molecular orbitals, and such a set has been calculated for B_4H_{10}.[153] The procedure was to construct extended-Hückel-type molecular orbitals and then maximize the electron populations in the bond regions. Pauling has suggested a similar approach in which each B—B 'bond' requires one valence electron and each hydrogen atom is bonded to the core by 1·75 valence electrons.[154] A more general approach to the bonding in so-called 'basket' molecules has been developed recently: the Hückel energies of B_4H_{10} were separately calculated from four topologically chosen basis sets.[62] This approach has been shown to be a logically correct extension of planar Hückel theory to three dimensions.[155]

The reactivities of the boron hydrides are also the subject of a topological approach: for B_4H_{10}, S_{N1} reactions are the most favoured at B(1) and S_{E1} reactions at the bridge protons.[156]

Physical Properties

Tetraborane(10) is a colourless compound with a boiling point close to the ambient temperature. Its physical properties have not received as much study as those of diborane(6). Stock reports[157] that the low thermal stability of B_4H_{10} and its tendency to decompose slowly into a mixture of other boranes, even below 0°C, makes the accurate determination of its physical properties difficult. Experimental vapour pressures for the liquid[157] consequently show some scatter, especially near the observed boiling point, which is close to 18°C and rather higher than the value of 16°C predicted by a semi-empirical relationship.[158] In spite of extensive compilations of thermodynamic properties of many boron compounds,[159–63] reliable data for B_4H_{10} are comparatively scant compared with those available for some higher boranes such as B_5H_9. A careful study of the vapour pressure of B_4H_{10} over the range −97 to −57°C has produced the vapour-pressure relationship

$$\log p_{\mathrm{Torr}} = -2831{\cdot}34/T - 15{\cdot}673 \log T + 50{\cdot}927$$

for the said range.[161] The entropy, heat capacity and certain other physicochemical properties have also been determined.[161,162]

Gunn and Green obtained ΔH_f° from what is undoubtedly the most reliable calorimetric value available for the heat of any reaction involving B_4H_{10}, i.e., explosion admixed with SbH_3:[164] their value for the enthalpy of formation at 25°C of B_4H_{10}, 13·8 kcal mol^{-1}, has been revised to 15·8 kcal mol^{-1} by Wagman *et al.*[160] to accommodate a revision of 0·5 kcal mol^{-1} per boron atom in the heat of transformation of amorphous to crystalline boron. A predicted value, obtained by means of a procedure due to Bauer for estimating the enthalpies of formation of boron compounds,[165,166] was 13·8 kcal mol^{-1} as derived from an empirical system of molecular entropies.[65] Another estimate was based on the average bond energies of a series of boron compounds and amounted to 14·0 kcal mol^{-1}.[167] The experimental value 15·8 kcal mol^{-1} corresponds by thermochemical computation to the value 1058·95 kcal mol^{-1} for the atomic heat of formation ΔH_a of B_4H_{10}. For comparison with this is the less convincing value 1017·00 kcal mol^{-1} obtained from a system of relationships between bond energy and bond length.[168]

Values for the physical properties of B_4H_{10}, including the free energy of vaporization,[169] are listed in Table V.

Table V.—Physical and Physicochemical Properties of Tetraborane(10)

Property	Numerical value	Unit	Reference
Melting point	$-120{\cdot}65 \pm 0{\cdot}1$	°C	161, 170
Boiling point	18	°C	157
Vapour pressure, 0°C	387 ± 1	Torr	157
Density of solid	0·70[(a)]	g cm^{-3}	159
Entropy of solid, $-120{\cdot}65$°C	$18{\cdot}38 \pm 0{\cdot}20$	cal K^{-1} mol^{-1}	161
Density of liquid, -35°C	0·56	g cm^{-3}	157
Heat capacity of liquid, $-102{\cdot}94$°C	26·809	cal K^{-1} mol^{-1}	161, 162
Entropy of liquid, $-98{\cdot}15$°C	$33{\cdot}01 \pm 0{\cdot}28$	cal K^{-1} mol^{-1}	161
Enthalpy of fusion	1·637	kcal mol^{-1}	161
Entropy of fusion	$10{\cdot}734 \pm 0{\cdot}05$	cal K^{-1} mol^{-1}	161
Enthalpy of vaporization, $-98{\cdot}15$°C	$7{\cdot}506 \pm 0{\cdot}150$	kcal mol^{-1}	161
Gibbs free energy of vaporization, 25°C	$-0{\cdot}204$	kcal mol^{-1}	169
Entropy of vaporization, $-98{\cdot}15$°C	$42{\cdot}89 \pm 0{\cdot}86$	cal K^{-1} mol^{-1}	161
Entropy of vaporization, at b.p.[(b)]	22·4	cal K^{-1} mol^{-1}	169
Enthalpy of formation of vapour, 25°C, 1 atm	15·8	kcal mol^{-1}	160

(a) Apparently calculated from the crystallographic data of Ref. 118.
(b) At an extrapolated b.p. lower than that listed above.

Tetraborane(10) is freely soluble in hydrocarbon solvents, including benzene, which, unlike solvents that contain multiple carbon-carbon bonds, does not react with B_4H_{10}. It is also soluble in carbon disulphide. On the other hand, liquid B_4H_{10} is immiscible with water; it floats on the surface while a slow hydrolysis proceeds.[1,2]

Physiological Properties

Tetraborane(10) has a peculiar and highly disagreeable odour. When highly diluted, the vapour has a smell reminiscent of chocolate. That the odour is still more unpleasant than that of diborane(6), is probably to be associated with its slower rate of hydrolysis on the moist mucous membrane of the nose. When inhaled, even a few bubbles of B_4H_{10} vapour cause headache and nausea.[2] Reviews on the toxicology of boron hydrides include those by Schrenk[37] and by Levinskas.[39] Rather little work has been carried out on tetraborane(10) itself, but its toxicity is thought to be similar to the toxicities of pentaborane(9) and the high-energy fuels based on that compound.[171–3] These are more toxic than diborane(6). There is evidence for the accumulation of such boron hydrides in the body,[174] and an upper toleration limit of 0·01 ppm has been given for repeated doses of B_5H_9, which rapidly attacks the central nervous system.[37] The LC_{50} for that compound is 18 ppm. The action and the safety limit of B_4H_{10} are likely to be similar.[38]

Charcoal is a poor absorbant for the vapours of the higher boranes, and soda-lime canisters have been recommended.[175]

Preparation

The methods of preparing tetraborane(10) have been critically reviewed.[12,26] The original method was based on the acid hydrolysis of magnesium boride;[1,2] this has been entirely superseded by methods that use diborane(6) as precursor,[26] which in turn may be prepared from commercial sodium tetrahydroborate $NaBH_4$, as described on pp. 69–73. The detailed studies in borane preparations carried out in American industrial laboratories, notably those of the Callery Chemical Company and Olin Mathieson Chemical Corporation, have been summarized.[11] A very detailed investigation of the preparation of B_4H_{10} itself was carried out at the Mathieson laboratories by DeLorenzo and Chick.[176] It is convenient to classify the various methods of preparation in the manner adopted below.

FROM METAL BORIDES

Stock and Massenez first obtained B_4H_{10} in 1912 by the reaction of dilute hydrochloric acid with magnesium boride.[1] The yields obtained in this work were very low (0·1–1·0 %). Furthermore, the product was contaminated with silanes, which made it less convenient to handle. The practical difficulties of these experiments led to the development of high-vacuum techniques which still form the basis of modern practice.[2] To provide larger quantities of tetraborane(10), a semi-automatic electric apparatus was devised for the decomposition of kilogram quantities of magnesium boride with hydrochloric acid.[157] If phosphoric acid is used in place of hydrochloric, the yield of B_4H_{10} rises to 11 %.[177, 178] Low yields of B_4H_{10} are obtained by treating aluminium and cerium borides with phosphoric acid, but, advantageously, the product is largely free of contaminants such as silanes.[179] Even when hydrochloric acid is used, purer samples of B_4H_{10} are obtained from beryllium boride than from its magnesium analogue.[180] The solution obtained by treating magnesium boride with caustic soda also yields B_4H_{10} when it is acidified.[181] Interestingly, yields of tetraborane(10) obtained by Stock with magnesium boride could not be reproduced by other investigators in 1954, apparently because of a variation in the composition of the boride.[182]

A comprehensive study has been made of the preparation of B_4H_{10} by the hydrolysis of borides, including those of Al, Fe, Ni and Mn, and the products formed in the reduction of boric oxide with Na, Li, Be, Mg and Ca.[183] The most advantageous yields are obtained when Mg is used as the reducing agent, but still better yields are obtained from magnesium boride prepared by heating Mg with amorphous boron. With phosphoric acid this material gives tetraborane(10) in a reported yield of 14·5 %, the highest ever claimed for a reaction commencing with a boride.[183] These results were confirmed and extended for the borides of Mn, Cr, Fe, Ni and Co.[184] Finally, the protonolysis of borides by ammonia and other solvents has been studied; this method generally gives poor results.[185] The mechanism of the acid hydrolysis of magnesium boride has been discussed.[186]

FROM DIBORANE(6)

After the pioneer work of Stock, other workers, notably the group led by Schlesinger, obtained diborane(6) by other methods (p. 69), so that this became much the most readily available boron hydride and could be used as a source of B_4H_{10}. Stock and Mathing had previously obtained B_4H_{10} by the pyrolysis of diborane in a flow apparatus consisting of a heated tube, a circulating pump and a trapping system.[187] After 21 h at 180°C, the yield of B_4H_{10} is 22 % with a 56 % conversion of B_2H_6: at 300°C lower yields are obtained.[157] After B_2H_6 (150 cm^3) had been allowed to stand exposed to light at room temperature for six months, it was found to contain a small amount of B_4H_{10} (0·6 cm^3) together with some B_5H_{11} and $B_{10}H_{14}$.[188] Conversely, other workers report that B_4H_{10} may be obtained in good yield by the storage of diborane(6) at room temperature.[10, 162, 189] Industrial reports on the pyrolysis of B_2H_6 under high pressure are available.[190, 191] Tetraborane yields of 86 % are obtained at 28 % conversion of the B_2H_6 when reaction is carried out at 250 atm and 90°C for 9 h,[190] while yields as high as 95 % at a 17 % conversion of B_2H_6 are obtained in 3 h by using pressures of 200 atm at 80°C.[191] Dillard was the first to report the use of this method;[192] a 20–35 % yield of B_4H_{10} was recorded for room-temperature reactions lasting several days.

A hot-cold concentric-tube reactor was developed for the preparation of tetraborane(10) and pentaborane(11) from diborane(6):[193] 80–95 % yields of B_4H_{10} are obtained when the B_2H_6 is passed at about 2 atm into a reactor with walls at 120 and −80°C separated by 1 cm.[194] Re-investigation of this reaction with the mass spectrograph originally led to the suggestion that a heptaborane species, B_7H_{13}, was formed in addition to the other boron hydrides previously observed,[195] but it now appears more likely that the supposed heptaborane was a relatively stable carbon-containing species.[81, 196]

There is no doubt that preparation from diborane(6) is the best method for the industrial or large-scale production of B_4H_{10}, and the following method,[26] which was developed by the Callery Chemical Company, is considered by them to be the preferred procedure.

Pure diborane(6) (2–2·5 lb) is condensed into a 1-gallon stainless-steel Hoke cylinder fitted with a 2200 lb in^{-2} safety valve. This is stored for 10 days at 25°C in a safe location, as a maximum pressure of 100 atm can be developed. The cylinder is cooled to −78°C and the H_2 with some of the B_2H_6 is allowed to escape until the pressure falls to 50 lb in^{-2}. The B_2H_6 is then distilled from the reactor at −50°C into a second cylinder at −78°C, using stainless-steel tubing, when the unreacted B_2H_6 (about 1·8–2·0 lb) is recovered. The residue is pumped through traps at −78 and −196°C. Repeated fractionation of the −78°C fraction produces about 170–175 g of B_4H_{10} (15 % yield). An apparatus for the continuous production of B_4H_{10} in the vapour phase has been described.[197]

It has been found that most common hydrogenation catalysts are unsatisfactory for the conversion of diborane(6) to higher boranes at 150–200°C, and optimum yields of tetraborane(10) (6 % only) have been obtained by the use of anhydrous alumina.[198] Other workers report that the controlled pyrolysis of B_2H_6 in the presence of dimethyl ether at 150°C leads to a 5·5 % yield of B_4H_{10}, but the principal product is $B_{10}H_{14}$.[199] Good yields are also reported from the pyrolysis of B_2H_6 in the presence of a liquid phase such as cyclohexane.[11] The complicated mechanism of this pyrolysis reaction has been discussed (p. 135). The experimental work has been recently reviewed and reinterpreted,[81] while the role of tetraborane(10) has been variously discussed by several workers.[200–5]

The conversion of B_2H_6 to higher boranes in a silent electric discharge received considerable attention during the high-energy-fuel programme.[11, 206–8] Tetraborane(10) can be prepared by subjecting diborane(6) at 180–250 Torr to a silent electric discharge of 15 000 V at −25 to 15°C. The yield is improved by diluting the B_2H_6 with helium or argon and by removing the hydrogen that is produced.[209] Yields of 7–36 % of very pure tetraborane(10) have been obtained by using a 16 000–25 000 V discharge and adopting a residence time of 1 min.[45] Yields as high as 40 % have been obtained at −153°C.[210] Additionally, workable yields of hexaborane(10) and nonaborane(15) may be obtained by this method.[210] The γ-irradiation of B_2H_6 using a ^{60}Co source has been shown to produce B_4H_{10} with a yield of 6 %.[211]

The 185 nm radiation of the mercury $6(^3P_1)$ emission spectrum promotes the conversion of B_2H_6 to B_4H_{10} in high yield. This work was originally carried out by two independent groups.[212–14] Recent deuteration studies confirm that a key step is the fission of a hydrogen molecule,[215, 216] so that the reaction corresponds closely to the simple overall equation

$$B_2H_6 \xrightarrow{h\nu} \tfrac{1}{2}B_4H_{10} + \tfrac{1}{2}H_2$$

which applies in principle to all of these diborane(6) conversions.

Small amounts of B_4H_{10} have been recorded during the gas-phase reaction of diborane(6) with pentaborane(9),[217, 218] with oxygen atoms at 25–100°C[219] and with $B_2H_4(PF_3)_2$ at room temperature.[220]

FROM HIGHER BORANES

Pentaborane(11), which is readily obtained in high yield if diborane(6) is passed through a U-tube at 115°C with a 3-minute residence time,[221] can be rapidly converted to tetraborane(10). The method is to heat a 10 : 1 mixture of H_2 and B_5H_{11} for 10 min in a bulb at 100°C:

$$B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + \tfrac{1}{2}B_2H_6$$

Under these conditions a 75 % yield of B_4H_{10} is obtained; prolonged heating leads to the formation of B_5H_9 and $B_{10}H_{14}$.[221, 222]

A small yield of B_4H_{10} has been obtained during the γ-ray radiolysis of B_5H_9 in the gas phase.[223] Traces of tetraborane(10) have also been recorded during the conversion of B_5H_{11} to ethylpentaborane(11) with ethylene.[224] An interesting observation is that B_5H_{11} is converted almost quantitatively to B_4H_{10} by hydrolysis in the gas phase at 0–25°C, when the reaction is complete in 1 min at a pressure of 15–50 Torr:[225–7]

$$B_5H_{11}+3H_2O \rightarrow B_4H_{10}+B(OH)_3+2H_2$$

Additionally, small quantities of B_5H_9 are formed. A similar conversion is effected by $(Me_2N)_2BH$. In this case the yield of B_4H_{10} is only 19 % and B_5H_9 is the main product.[227, 228] Small quantities of B_4H_{10} have been obtained during carborane syntheses from B_5H_9 and alkynes in the presence of 2,6-dimethylpyridine.[79] Hexaborane(12) is similarly hydrolysed almost quantitatively to B_4H_{10}, but in the corresponding reaction with dimethyl ether B_5H_9 is formed instead.[229] There is a report of a degradation of $B_{10}H_{14}$ that is suitable for the small-scale preparation of B_4H_{10} and B_6H_{10}: $B_{10}H_{14}$ is known to be smoothly converted to $B_9H_{14}^-$ salts by amines;[230] when $[NHEt_3][B_9H_{14}]$ is treated with polyphosphoric acid at room temperature *in vacuo*, B_4H_{10} is obtained in 37 % yield.[231]

FROM TETRAHYDROBORATES

Because of their availability and ease of handling, the potential use of alkali metal tetrahydroborates as starting materials for the preparation of tetraborane(10) is of great interest. But there appears to be only one chemical process known in which B_4H_{10} results as a major product in a single-stage operation, namely the reduction of B_2Cl_4 with lithium or aluminium tetrahydroborate:[232, 233]

$$B_2Cl_4+4LiBH_4 \rightarrow 4LiCl+B_2H_6+B_4H_{10}$$

This reaction is of little value, however, because B_2Cl_4 is not a readily accessible compound, nor is it convenient to handle. Other direct methods do not produce B_4H_{10} as a major product, but as a component of a mixture of boranes from which the B_4H_{10} must be separated. Possibly the compound is produced wholly or largely *via* diborane(6), which is usually the main product (pp. 69–72, 78). Thus, if $NaBH_4$ is heated with BF_3 or BCl_3 to 200–250°C without a solvent, a 99 % conversion of the $NaBH_4$ to a mixture of boranes containing some B_4H_{10} is realizable.[234] Similarly electrolysis of an ionic tetrahydroborate such as $NaBH_4$ dissolved in a melt of fused salts (typically a mixture of LiCl, NaCl, KCl and $AlCl_3$) causes a mixture of boranes to be liberated at an inert anode.[235] Diborane(6) predominates, but the amounts of higher boranes produced above 250°C are significant. Difficulties are likely to be caused by the appearance of molten alkali metals at the cathode.

Of much greater serviceability are indirect preparations from tetrahydroborates, which may be accomplished *via* diborane(6)—which is readily released from them in a number of ways (pp. 69–73)—or, better, via the octahydrotriborate ion $B_3H_8^-$. The latter is readily prepared from a diglyme solution of $NaBH_4$ at 100°C by the action of B_2H_6,[236] BF_3[236] or, simplest of all, elemental iodine[237] (p. 172). The octahydrotriborate(1−) ion is readily isolated and conveniently stored as the tetramethylammonium salt $Me_4NB_3H_8$.[236] When this compound is dropped into polyphosphoric acid under vacuum, B_4H_{10} is obtained in about 43 % yield,[229] together with a little B_6H_{12} and traces of other boranes:

$$3BH_4^- + I_2 \xrightarrow[100°C]{\text{diglyme}} B_3H_8^- + 2I^- + 2H_2$$

$$2B_3H_8^- \xrightarrow[40°C]{H_4P_2O_7} \underset{(43\,\%)}{B_4H_{10}} + \text{other boranes}$$

Since the B_4H_{10} is readily separated by vacuum fractionation, this new route is doubtless the most convenient preparative method available to date for the small-scale laboratory preparation of this compound.

FROM BORON TRIHALIDES

Because the reduction or direct hydrogenation of boron trichloride leads mainly to the formation of diborane(6) (pp. 75, 76, 77), it is presumably correct to assume that the production of any B_4H_{10} proceeds, at least in part, *via* B_2H_6. It is however not necessary to isolate the latter. Thus an early patent claims the preparation of various boranes, including B_4H_{10}, by the reduction of a boron trihalide with hydrogen at 150–400°C in the presence of an active metal hydride.[238] Later patents deal with production of mixtures of boranes from the interaction of BF_3 or BCl_3 with $NaBH_4$ in the absence of a solvent. At 250°C some B_4H_{10} occurs among the products,[234] but if aluminium chloride is used as a catalyst the yield of tetraborane(10) is smaller and the main product is diborane(6).[239] This change in the relative proportion of the products may be a consequence of the lower temperature needed.

OTHER METHODS

Stock and Pohland prepared B_4H_{10} by a Wurtz-type synthesis from B_2H_5I and sodium amalgam.[240] B_2H_5I is prepared by the reaction of B_2H_6 with HI at 50°C:

$$2B_2H_5I + 2Na \rightarrow B_4H_{10} + 2NaI$$

This reaction has been reinvestigated:[241] yields of B_4H_{10} in the range 52–70 % are reported together with traces of B_5H_9, B_5H_{11} and B_6H_{12} when the reaction is carried out at low temperatures, but this work adds rather little to the earlier results.[240]

The hydrolysis of the boron suboxide BO over a 2-hour reaction period enables 0·3 % of the boron to be recovered as boron hydrides, mainly B_4H_{10} and B_5H_9 in a 5:1 molar ratio.[242, 243] The magnesium boride which Wiberg and Schuster treated with H_3PO_4, in order to obtain B_4H_{10} in 11 % yield, was not fully deoxygenated.[178] Stock records the appearance of the characteristic odour of traces of B_4H_{10} during various reactions;[2] these include acidifying a solution of potassium 'hypoborate'[244] (later shown to consist largely of tetrahydroborate[245]), oxidizing $B_{10}H_{14}$ with potassium permanganate solution,[246] and acidifying a sodium hydroxide solution of the bromination products of decaborane(14).[181]

PREPARATION OF ISOTOPICALLY LABELLED SPECIES

The number of conceivable stereoisomers among the isotopically substituted species of tetraborane(10) is very large. Unfortunately this has not previously been calculated, as B_4H_{10} was omitted from a treatment in which the total number of isomers of derivatives of the higher boranes has been derived from the molecular symmetry of the individual borane.[247, 248] But by following the same method we have calculated the number of possible stereoisomers for all possible kinds of substitution of any number of the six terminal hydrogen atoms of the B_4H_{10} molecule of C_{2v} symmetry. The number of enantiomorphic pairs of isomers were obtained by considering only the proper rotation (C_2): this gives the total number of isomers for substitution at the terminal hydrogen atoms as listed in Table VI. Considering deuterium substitution only, the total number of molecular species obtained from the Table is $2(a_6 + a_5b + a_4b_2) + a_3b_3$, i.e., 36. If substitution of the four bridge hydrogen atoms is also considered, the total number of molecular species is much larger.

Table VI.—Number of Isomers of Derivatives of Tetraborane(10) Substituted at the Terminal Hydrogen Atoms

Compound type	Total isomers	Enantiomeric pairs
a_6	1	0
a_5b	3	0
a_4b_2	9	2
a_3b_3	10	4
a_4bc	15	4
a_3b_2c	30	10
$a_2b_2c_2$	48	18
a_3bcd	60	24
a_2b_2cd	90	38
a_2bcde	180	78
$abcdef$	360	180

The reaction of B_5H_{11} with D_2O in a closed tube at 0°C gives B_4H_9D: n.m.r. and infrared evidence shows that the deuterium is originally in one of the four bridge positions (Fig. 2), but at room temperature scrambling of all of the hydrogen atoms occurs.[128] The species μ,1-$B_4H_8D_2$ obtained by the reaction of B_4H_8CO with D_2 requires only 30 min in the vapour phase at 25°C for complete scrambling of the deuterium.[86, 104] Another isotopic isomer of $B_4H_8D_2$, probably 1,3-$B_4H_8D_2$, has been prepared by the reaction of B_4H_{10} with B_2D_6 at 45°C and low pressure;[48] this reaction has been studied kinetically (p. 224).[84]

Isotopic labelling of the boron atoms is also possible. Boron-labelled tetraborane(10) has been prepared by two distinct routes.[249, 250] In the reaction between $Na{}^*B_3H_8$, ${}^nB_2H_6$ and HCl ($^*B = 96\ \%\ {}^{10}B$, ${}^nB = B$ of normal isotopic distribution), the ${}^nB$ was found exclusively in the 2 position of the B_4H_{10} (i.e. as part of one of the BH_2 groups).

$$Na{}^*B_3H_8 + HCl + \tfrac{1}{2}{}^nB_2H_6 \rightarrow NaCl + 2\text{-}{}^nB{}^*B_3H_{10} + H_2$$

On treatment of ${}^nB_2Cl_4$ with $Al({}^*BH_4)_3$ preferential enrichment of ${}^nB$ at the basal 1 and 3 positions (65 % ${}^nB$) was observed.

$$3{}^nB_2Cl_4 + 4Al({}^*BH_4)_3 \rightarrow 3{}^nB_2{}^*B_2H_{10} + 3{}^*B_2H_6 + 4AlCl_3$$

Analysis

For the determination of its formula, Stock originally analyzed tetraborane(10) in more than one way.[1] One method depended upon complete thermal degradation at 500°C to the elements, whereupon the boron was dissolved in nitric acid and determined by titration of the boric acid produced, while the hydrogen was determined from its volume and from the change in volume on sparking with an excess of air: the other methods depended on hydrolysis with water and with sodium hydroxide solution:[157]

$$B_4H_{10} + 12H_2O \rightarrow 4B(OH)_3 + 11H_2$$

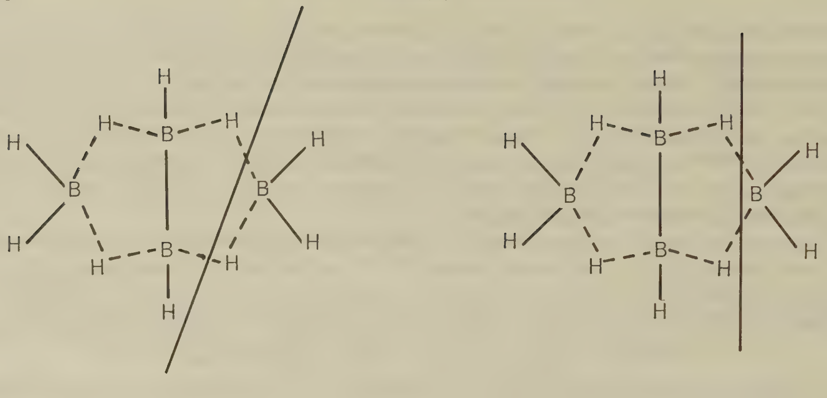
The density of the gas provided the molecular weight.

In more recent times, several workers have discussed methods of analyzing B_4H_{10} in the presence of other boranes. The use of a LeRoy fractionation column at low temperature has been suggested,[251] as have methods based on gas-liquid chromatography.[252, 253] A thin-layer chromatographic method has also been described; a direct technique is not possible, but the products with triethylamine, $Et_3N.BH_3$ and $Et_3N.B_3H_7$, are conveniently separated on silica gel.[254] It is a remarkable testimony to the experimental skill of Stock and his co-workers, that such techniques merely supplement the vacuum-line techniques for handling tetraborane(10) that were developed by them half-a-century earlier.[2]

Chemical Properties

Many of the reactions of tetraborane(10) were originally studied by Stock[2] and made the subject of a detailed industrial report published at a later date.[176] At about the same time, Burg summarized the chemical behaviour and bonding of boranes and their derivatives.[35, 36, 255] Additionally a detailed classification of boron hydride reactions has been undertaken,[34] in which a distinction is made between BH_3 cleavage, $BH_2{}^+$ cleavage, BH_3 three-centre addition, loss of bridging hydrogen atoms, addition of a proton, intramolecular hydrogen exchange, electron addition, loss of H_2, condensation and polymerization reactions, substitution of hydrogen and substitutional attack by electron-donor reagents. For tetraborane(10) four principal types of reaction have been reported, namely symmetric cleavage, asymmetric cleavage, loss of protonic bridging hydrogen atoms and the loss of molecular hydrogen:[33] however, it is now known that cleavage of molecular hydrogen is not important at moderate temperatures, except in the presence of a suitable second substance such as carbon monoxide.

Symmetric and asymmetric modes of cleavage for B_4H_{10} are illustrated in Fig. 7. Symmetric cleavage leads to $BH_3 + B_3H_7$, while asymmetric cleavage produces the ions $BH_2{}^+$ (in a coordinated form) and $B_3H_8{}^-$. These cleavage modes correspond to the symmetric and asymmetric cleavage of diborane(6) to $BH_3 + BH_3$ and to $BH_2{}^+$



(a) (b)

FIG. 7.—Cleavage modes of B_4H_{10}: (*a*) symmetric, (*b*) asymmetric

(coordinated) plus BH_4^- respectively. There is no known case of asymmetric fission of tetraborane(10) to $BH_4^- + B_3H_6^+$.

Like other boranes B_4H_{10} is a Lewis acid: it is a stronger acid than B_5H_9, but weaker than $B_{10}H_{14}$.[112]

A topological approach to the reactivities of the boron hydrides indicates that for B_4H_{10} nucleophilic substitution should occur most readily with the terminal hydrogen atoms attached to boron atoms B(1,3) and electrophilic substitution at the bridge positions.[156]

INTRAMOLECULAR EXCHANGE

Early studies of the kinetics of isotope exchange between tetraborane(10) and diborane(6) showed that the kinetics could not be explained unless an additional intramolecular rearrangement of the B_4H_{10} was assumed to occur simultaneously.[84, 85] Whether intramolecular boron exchange occurs in B_4H_{10} has not so far been clarified, although positive evidence for this exists in the case of some higher boranes. It is however certain that the hydrogen atoms of B_4H_{10} undergo intramolecular exchange, and that with deuterium-labelled samples complete randomization occurs within 30 min at room temperature.[86] N.m.r. studies at high field strength have now shown that this occurs at two different rates.[256] The faster exchange process involves the four bridge hydrogen atoms and four of the terminal hydrogen atoms. The slower process also involves the bridge atoms and the remaining two hydrogen atoms, which are situated on the 2,4 boron atoms, though it has not been possible to establish which of the two non-equivalent terminal hydrogen atoms of the BH_2 groups are associated with the slower rate. A tentative attempt has been made to explain the two types of exchange in terms of different rotations of parts of the molecule about the boron atoms.[256]

THERMAL DECOMPOSITION

Tetraborane(10) is the least stable of the boranes isolated by Stock. It decomposes slowly at room temperature,[157] and more rapidly when warmed: even at 0°C and below, the accurate measurement of the vapour pressure is rendered difficult through decompositions. The compound must therefore be stored at reduced temperatures. At 100°C the initial decomposition products are principally diborane(6) and pentaborane(11) (see Fig. 10), but since hydrogen is also produced the B_5H_{11} first formed soon begins to disappear, so that with somewhat longer times of heating the chief products are H_2 and B_2H_6, together with some less volatile liquid and solid hydrides.[257–9] The mechanism is discussed on pp. 218–223. Pyrolysis at 110°C, has led to the observation of a small quantity of B_6H_{12} (in about 1% yield) among the products.[260]

The rate of decomposition increases once the change has begun.[257] Sunlight has no significant influence upon the decomposition, but ultraviolet light produces a strong acceleration without changing the character of the process.[246] Tetraborane(10) seems to decompose more rapidly when it contains traces of silicon hydrides.[157] At higher temperatures the decomposition proceeds rapidly, forming H_2, B_2H_6, B_5H_9, $B_{10}H_{14}$ and non-volatile colourless or yellow hydrides. To obtain a good yield of diborane, Stock heated B_4H_{10} for some hours at 90°C:[157] at 200°C a good yield of B_5H_9 is obtained, and decomposition into the elements commences at 300°C. The formation of the pentaboranes precedes that of the solid hydrides.[157, 238, 257, 261] Stock reports that the hydrogen released by the spontaneous decomposition of B_4H_{10} reduces Si_2H_6 to SiH_4.[157]

A reinvestigation of the pyrolysis of B_4H_{10} demonstrated the formation of B_5H_9, B_5H_{11}, B_6H_{12}, B_8H_{18}, B_9H_{15} and $B_{10}H_{14}$ under mild conditions.[262, 263] Mass spectrometric investigations support these findings.[143] Conversely, Neff reported that decaborane(14) is produced with only minor formation of other boranes of high molecular weight by the pyrolysis of tetraborane(10) at 65°C and 715 lb in^{-2} pressure.[264] In another study the formation of B_6H_{10} in high yield has been recorded.[265] Kinetic studies of the pyrolysis of tetraborane(10) under various conditions have been carried out[258, 259, 266, 267] (see p. 219).

Exposure of B_4H_{10} to an electric spark produces a spontaneously inflammable liquid, solid hydrides, elemental boron and hydrogen.[2]

Unlike diborane(6), B_4H_{10} is not stabilized by storing with hydrogen; even though some modes of decomposition are inhibited,[259] B_4H_{10} reacts slowly with hydrogen,[221] the principal product being B_2H_6. The reaction is not a simple molecular one, as will be seen from the discussion of the mechanism on pp. 219–223.

CO-PYROLYSIS REACTIONS

The co-pyrolysis of B_4H_{10} with B_2H_6 was first reported by Pearson and Edwards,[259] and has been further studied since.[266] Both compounds are consumed to produce pentaborane(11) and hydrogen. The rate is however independent of the concentration of B_2H_6, so that the reaction is not simply one involving a direct interaction of B_4H_{10} and B_2H_6 molecules. The mechanism is discussed elsewhere[81] (p. 223). The reaction is moreover essentially reversible, and several groups of workers have investigated the pseudoequilibrium between B_2H_6, B_4H_{10}, B_5H_{11} and H_2 in the gas phase.[194, 202, 222] In one study of this system, as represented by the overall equilibrium equation

$$2B_5H_{11}(g)+2H_2(g) \rightleftharpoons 2B_4H_{10}(g)+B_2H_6(g)$$

and confined to the temperature range 100–140°C, the enthalpy change was determined to be $-7{\cdot}56$ kcal mol^{-1} and the entropy change $-19{\cdot}5$ cal K^{-1} mol^{-1}.[202] This system is however peculiarly complex, because material is continually being removed in the form of B_5H_9, $B_{10}H_{14}$ and other higher boranes.[222] Todd and Koski investigated deuterium-exchange reactions between diborane(6)-d_6 and tetraborane(10): they found implication of two competing reactions, as set forth on p. 224, and concluded on rather tentative evidence that two of the hydrogen atoms of the tetraborane are exchanged more rapidly than the remaining eight.[84] Conversely, there was no observable exchange reaction between B_4H_{10} and D_2 at 45°C,[84, 85, 268] and the formation of the intermediate B_3H_7 was suggested.[85] Also, when a mixture of B_4H_{10} and H_2 is treated with shock waves, hexaborane(12) is formed,[269] itself a strong indication of B_3H_7 formation.[81]

The co-pyrolysis of B_4H_{10} and B_5H_9 at 65°C and high pressure is a convenient method for the formation of $B_{10}H_{14}$ in good yield.[270] Several higher boranes, including octaborane(12), are obtained during the co-pyrolysis of B_4H_{10} and i-B_9H_{15} under mild conditions.[263]

When B_4H_{10} is co-pyrolyzed with a second substance, the latter is frequently decomposed at a lower temperature or at a faster rate than in the absence of tetraborane. This effect, which is already very noticeable when the second substance is B_2H_6, is likely to be still more marked when the second substance is a boron-free compound. Hydrocarbons constitute a case in point. Thus ethane disappears completely within 4 h when heated at 115°C with an excess of B_4H_{10}: apart from B_2H_6, B_5H_9 and H_2, the only product is a non-volatile, yellowish white, crystalline solid containing both carbon and boron as well as hydrogen.[157] With acetylenes, tetraborane gives rise to volatile carboranes, a reaction of sufficient importance to discuss separately below (p. 218). With disilane, products containing both silicon and boron are not produced, but Si_2H_6 is converted to SiH_4 by decomposing B_4H_{10}.[157]

SUBSTITUTION BY ORGANIC GROUPS

So far as is known, only the terminal hydrogen atoms of tetraborane(10) are capable of substitution by organic groups. The situation thus resembles that for diborane(6). In the case of B_4H_{10} the total number of simple organic derivatives possible with a maximum of six different substituents can be ascertained by reference to Table VI, though only singly and doubly substituted derivatives have been characterized to date. Certain derivatives of this type are listed in Table VII.

Table VII.—Physical Properties and References to Spectra of Some Substituted Derivatives of Tetraborane(10)

Compound	Physical property	Reference	References to spectra		
			Infrared	N.m.r.	Mass
2-B_4H_9Me	m.p. −126°C	271	220, 271–273	220, 271, 272	220, 271–273
1,2-$B_4H_8Me_2$			220, 271	220, 271	220, 271
2,2-$B_4H_8Me_2$	b.p. 72°C (extrapolated)	274	220, 271, 274	220, 271, 274	220, 271, 274
2,4-$B_4H_8Me_2$	m.p. $-92\cdot5\pm0\cdot3$°C	271	220, 271	220, 271	220, 271
2,4-$B_4H_8C_2H_4$	b.p. 84°C (extrapolated)	275	93, 94	94, 275	275
	vapour-pressure relation: $\log p_{\mathrm{Torr}} = 10\cdot222\,89 - 3077\cdot509/T + 162\,748\cdot8/T^2$	275			
	$\Delta H_v^{298\cdot15}$ 9·083 kcal mol^{-1}	275			
2,4-$B_4H_8C_2H_3Me$			94	94	
2,4-$B_4H_8(CHMe)_2$			94	94	
2-B_4H_9Br	m.p. $-37\cdot1\pm0\cdot5$°C	276	277	276, 278	
	b.p. 110°C (extrapolated)	276			
	vapour-pressure relation:[(a)] $\log p_{\mathrm{Torr}} = 7\cdot951\,93 - 1928\cdot05/T$	276			

[(a)] Recalculated from the published equation $\ln p_{\mathrm{mm}} = 18\cdot31 - 8822/RT$.

One method of producing alkyl-substituted tetraboranes is to treat B_4H_{10} with alkyldiboranes. The first product from this method, shown to contain B, C and H, was the subject of a patent.[279] More precise work has shown that heating B_4H_{10} to 45°C with either of the methyldiboranes B_2H_5Me or 1,2-$B_2H_4Me_2$ yields 2-methyltetraborane B_4H_9Me.[272, 273, 280] At 100°C, however, the isolated products were not substituted tetraboranes, but the pentaborane(11) derivatives $B_5H_{10}Me$ and $B_5H_9Me_2$. No corresponding reactions between B_4H_{10} and ethyldiboranes were observed by other workers.[281]

Another effective alkylating reagent is dimethylmercury $HgMe_2$: 5 minutes' reaction time with B_4H_{10} at 50°C was observed to give a 68 % yield of 2-B_4H_9Me.[282] Some BMe_3 and methyldiboranes were also obtained from this reaction. Which other metal alkyls behave similarly has not yet been established, but it can be stated that simple trialkylboranes are not effective. Thus when B_4H_{10} is allowed to react with excess BEt_3 for 24 h at room temperature and then for 1 h at 50°C a polymeric material of formula $(BH_2)_x$ $(x > 10)$ is obtained, a reaction which B_4H_{10} has in common with B_5H_{11} and B_6H_{12}.[283, 284]

Alkyltetraboranes can also be formed from triborane(7) adducts and from octahydrotriborate(1−) salts. The reaction of the dimethyl ether adduct $B_3H_7.OMe_2$ with 1,2-$B_2H_4Me_2$ at −13°C has resulted in the isolation of 1,2-$B_4H_8Me_2$, 2,2-$B_4H_8Me_2$ and 2,4-$B_4H_8Me_2$,[220, 271] as well as the already known 2-B_4H_9Me. The dimethyl derivative 2,2-$B_4H_8Me_2$ has also been prepared in a boron-insertion reaction of potentially great synthetic interest from a slurry of NaB_3H_8 and BMe_2Cl at −30°C:[274]

$$NaB_3H_8 + BMe_2Cl \rightarrow NaCl + 2,2\text{-}B_4H_8Me_2$$

On treatment of the product with ammonia or methylamine, it undergoes asymmetric cleavage in which $[Me_2B(base)_2]^+$ ions but no $[BH_2(base)_2]^+$ compounds are formed.[286]

Even pentaborane(11) can be used as a starting material for the production of substituted tetraboranes. Thus, although ethyltetraboranes have not so far been produced directly from tetraborane(10), B_4H_9Et has been prepared by passing B_5H_{11} and ethylene over aluminium chloride at room temperature.[285] When B_4H_9Et is heated with diborane(6) for 3 h at 140°C, ethyldecaborane $B_{10}H_{13}Et$ is obtained in high yield.[287]

Cyclopropanes are also serviceable as alkylating agents for B_4H_{10}, since the latter effects a hydroboration reaction with C—C bond cleavage at about 80°C: the borane residue becomes attached to the least sterically hindered carbon atom. With 1-methylnorcarane, reaction is 15 % of complete in 15 min at 82°C.[288] In this respect B_4H_{10} behaves like B_2H_6 as noted on p. 103, and has a similar or slightly enhanced reactivity.

With ethylene, on the other hand, the reaction is not strictly simple hydroboration, since hydrogen is eliminated. Stock and Kuss reported that when ethylene is warmed with B_4H_{10} to 50°C over mercury, a white sublimate is formed which explodes when rubbed with filter paper.[157] Ethyltetraborane does not behave in this way. Other workers have carried out the reaction under different conditions, namely at 100°C over an aluminium chloride catalyst in a hot-cold reactor at atmospheric pressure, and obtained a volatile oil of vapour pressure 14·5 Torr at 0°C and formula $B_4H_8C_2H_4$ in 70 % yield:[93, 289]

$$B_4H_{10} + C_2H_4 \rightarrow B_4H_8C_2H_4 + H_2$$

It is unquestionably one of the most interesting derivatives of tetraborane(10), having been shown to possess a unique polycyclic bridge structure with a dimethylene chain linking boron atoms 2 and 4. It is therefore 2,4-(1,2-ethanediyl)tetraborane(10), formerly known as dimethylenetetraborane. The structure of this elegant basket molecule is depicted in Fig. 8. When the same reaction is carried out with ethylene-d_4, all of the deuterium is found in the dimethylene bridge system.[290] This observation points clearly to a reaction which proceeds by the simultaneous formation of both B—C bonds

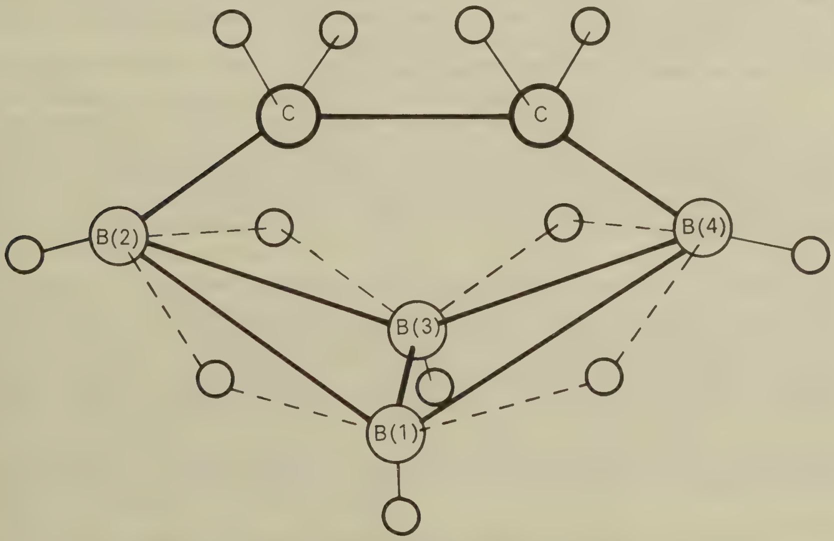


Fig. 8.—Basic structure of 2,4-(1,2-ethanediyl)tetraborane(10) $B_4H_8C_2H_4$, also known as dimethylenetetraborane(10). The larger light circles represent boron atoms, heavy circles carbon atoms, small circles hydrogen atoms

accompanied by the elimination of H_2 from the borane moiety, rather than *via* B_4H_9Et followed by ring closure with concomitant loss of hydrogen. It must therefore be written

$$B_4H_{10}+C_2D_4 \rightarrow B_4H_8C_2D_4+H_2$$

The reaction of ethylene with B_5H_{11} has also produced 2,4-$B_4H_8C_2H_4$, though in small yield.[224] Also known are C-methyl derivatives of the latter compound that have been produced by the reaction of 1-B_4H_8CO with olefins.[94]

N.m.r. and mass-spectral data have been obtained,[275] and the particular value of the n.m.r. observations in the characterization of this compound has been discussed.[129] In the 12·8 MHz ^{11}B n.m.r. spectrum, the low-field triplet of B_4H_{10} is transformed into a doublet ($J_{BH}=130$ Hz), which is shifted to -4 ppm, indicating alkyl-substitution at the 2 and 4 positions of B_4H_{10}. The high-field doublet has a similar position and fine structure in both B_4H_{10} and 2,4-$B_4H_8C_2H_4$ (39 ppm, 145 Hz). The ^1H spectrum of 2,4-$B_4H_8C_2H_4$ is rather complicated, but it is compatible with the foregoing basket structure.[275] Also compatible with the structure are the known degradation and addition reactions. On treatment of 2,4-$B_4H_8C_2H_4$ with a 30% solution of hydrogen peroxide, ethylene glycol is found among the products, while with methanol it undergoes an interesting alcoholysis reaction:[289]

$$2,4\text{-}B_4H_8C_2H_4+10MeOH \rightarrow (MeO)_2BCH_2CH_2B(OMe)_2+2B(OMe)_3+9H_2$$

Lewis bases effectively cleave the compound: whereas ammonia and trimethylamine cause extensive disruption of the boron cagework, trimethylphosphine merely effects a symmetric-type cleavage:[291]

$$B_4H_8C_2H_4+2PMe_3 \rightarrow Me_3P.BH_2C_2H_4B_3H_6.PMe_3$$

In none of these reactions does cleavage of the C—C bond occur.

The compound originally designated 'ethynyltetraborane' and prepared in the high-pressure co-pyrolysis of pentaborane(9) and acetylene at 250°C[292] is in fact the carborane *nido*-$B_4C_2H_8$. None of the 4-boron-carboranes will be discussed here, as they are described fully in another section of this book (p. 450).

SUBSTITUTION BY OTHER GROUPS OR ATOMS

The paucity of known examples of substituted tetraborane(10) derivatives containing other substituents (cf. Table VII), relative to the corresponding number known for diborane(6) (p. 85), is to be attributed mainly to the circumstance that B_4H_{10} has not yet been subjected to the same intensity of study as B_2H_6. Its readier cleavage by reagents that are also donors may also be a contributing factor.

The bromine derivative 2-B_4H_9Br has been prepared by the action of Br_2 on B_4H_{10} at -15°C.[248, 276, 278] The compound melts at -37°C and has an extrapolated boiling point of 110°C. In this compound, as with the diborane analogue B_2H_5Br described on pp. 98–99, the bromine is definitely substituted at a terminal position. In the 19·3 MHz ^{11}B n.m.r. spectrum there is a doublet at 1·5 ppm ($J=149$ Hz), a triplet at 10·0 ppm ($J=130$ Hz) and a second doublet at 34·7 ppm ($J=160$ Hz), these peaks exhibiting relative intensities close to the ratio 1:1:2 expected for a 2-substituted derivative. The corresponding iodo derivative has not been prepared: iodine is much less reactive, but in the presence of methanol it causes complete degradative alcoholysis, as seen on p. 217. Chlorine, on the other hand, is too reactive, and would presumably react destructively with tetraborane(10) as it does with the other boranes. The reaction of anhydrous HCl at room temperature has been investigated and found to be very slow, even in the presence of aluminium chloride, which lacks the expected catalytic effect: the only chlorinated product that has been observed on interrupting this reaction is BCl_3 without detectable amounts of B_4H_9Cl.[2, 177] Halogen exchange with 2-B_4H_9Br does not appear to have been attempted. On heating, 2-B_4H_9Br forms B_2H_6 and $BHBr_2$: it does not react with ethylene at -10°C, but reacts with $HgMe_2$ to form methyldiboranes.[277]

If it is possible to substitute B_4H_{10} with univalent groups such as —NR_2 or —SR, they would probably occupy bridge positions, as in the case of substituted diboranes (pp. 92, 97); but it is not yet known whether bridge-substituted derivatives of tetraborane(10) are capable of existence.

REACTIONS WITH METALS AND METAL COMPOUNDS

Stock reported originally that tetraborane(10) in excess reacts with sodium amalgam to form the involatile solid product $B_4H_{10}.2Na$.[177] The greater part of the tetraborane can be recovered from this product by treatment with hydrogen chloride. Some of the complexities of these experiments have been described.[2] A similar product $B_4H_{10}.2K$ is prepared from potassium amalgam.[293,294] It was considered that such compounds are really salts, to be written, e.g. $K_2B_4H_{10}$. At 170°C this compound reportedly loses H_2 to give a second compound of composition $K_2B_4H_8$; further hydrogen is lost at temperatures above 200°C to give, at 450°C, the species $K_2B_4H_6$, and at still higher temperatures yet other products. On treatment with hydrogen chloride, $K_2B_4H_{10}$ liberates diborane(6) in good yield, as well as B_4H_{10}.[294] $K_2B_4H_{10}$ has been considered to be a mixture of products of a type similar to '$K_2B_2H_6$' obtained from B_2H_6[295] and in turn believed to be a mixture containing KBH_4.

If tetraborane(10) in ether is treated with sodium amalgam, NaB_3H_8 is obtained in good yield, together with diborane and polymeric material:[296]

$$2B_4H_{10}+2Na(\text{amalgamated}) \rightarrow 2NaB_3H_8+\tfrac{1}{2}B_2H_6+\frac{1}{x}(BH)_x$$

Additionally B_4H_{10} reacts smoothly with NaH or $NaBH_4$ in ether to give NaB_3H_8 quantitatively with respect to sodium:[296]

$$NaH+B_4H_{10} \rightarrow NaB_3H_8+\tfrac{1}{2}B_2H_6$$
$$NaBH_4+B_4H_{10} \rightarrow NaB_3H_8+B_2H_6$$

No studies with lithium or divalent metals have been reported. The reaction of B_4H_{10} with AlH_3 is however given as a convenient method for the preparation of aluminium tetrahydroborate $Al(BH_4)_3$.[297] Metal alkyls deprotonate B_4H_{10} to give $B_4H_9^-$ salts at low temperatures [108–12] (see p. 192). In solution $KMnO_4$ is converted to MnO_2 by B_4H_{10}, while nickel salts are converted under alkaline conditions to nickel boride Ni_2B.[2]

REACTIONS WITH BORON COMPOUNDS

The reaction of tetraborane(10) with other boranes results in borane interconversions and has already been described on p. 209. However, reaction with substituted diboranes may lead to substituted derivatives of B_4H_{10} (see p. 210). Little is known about the behaviour of B_4H_{10} with other types of boron compounds. However, it reacts with $NaBH_4$ to form NaB_3H_8 as mentioned above; also at low temperatures it interacts with bis(dimethylamino)borane $BH(NMe_2)_2$ to form an adduct[227]

$$B_4H_{10}+BH(NMe_2)_2 \xrightarrow{-78°C} B_4H_{10}.BH(NMe_2)_2$$

It is not known for certain whether this is a rare example of a true coordinated molecular adduct of tetraborane(10), nor is it known whether the B_4H_{10} moiety is linked to the boron or one of the nitrogen atoms of the aminoborane. That it is more likely to be the former, is indicated by the formation of B_5H_9 in 25 % yield on decomposition during warming to −15°C.

REACTIONS WITH COMPOUNDS OF CARBON AND SILICON

Knowledge concerning the behaviour of B_4H_{10} with carbon compounds is limited. We are concerned here with reactions leading to the formation of a B—C bond. The reactions of B_4H_{10} with a number of organic compounds are described elsewhere, namely those with ethane (p. 209), cyclopropanes (p. 211, ethylene (p. 211) and acetylenes (pp. 218–219).

With trimethylsilylacetylene $Me_3SiC{\equiv}CH$, involatile products along with B_2H_6 and B_5H_9 are obtained.[298] The reactions of B_4H_{10} with organoboranes (p. 210) and dimethylmercury (p. 210) have also been discussed.

When B_4H_{10} is pyrolysed in the presence of carbon monoxide, tetraborane(8) carbonyl can be isolated as an intermediate:[83,95]

$$B_4H_{10}+CO \rightarrow B_4H_8CO+H_2$$

This equation, however, refers only to the overall reaction.

Tetraborane(10) reacts with sodium cyanide in dimethoxyethane a little below room temperature to form sodium salts of adducts with the cyanide ion, namely of $B_3H_7CN^-$ and $H_3BCNBH_3^-$.[299]

$$2B_4H_{10}+3NaCN \xrightarrow{C_4H_{10}O_2} 2NaB_3H_7CN+NaH_3BCNBH_3$$

The reaction of B_4H_{10} with alcohols is described on p. 217.

Little is known concerning the action of tetraborane(10) on silicon compounds and nothing about its behaviour towards germanium compounds. It apparently does not react with silane; but in the presence of decomposing B_4H_{10} it was noted that Si_2H_6 is converted to SiH_4.[157] No boron-silicon compounds were isolated from this reaction.

REACTIONS WITH COMPOUNDS OF NITROGEN AND PHOSPHORUS

Tetraborane(10) is to be regarded as a Lewis acid.[300] Since, however, the acidic properties of its cleavage products B_3H_7, BH_3 and BH_2^+ greatly exceed those of the parent molecule, it is not surprising that Lewis bases (L) promote cleavage of B_4H_{10}:

$$\begin{tikzcd} & L.BH_3+L.B_3H_7 \\ & \text{(symmetric)} \\ B_4H_{10}+2L \arrow[uur] \arrow[ddr] & \\ & BH_2L_2^+ + B_3H_8^- \\ & \text{(asymmetric)} \end{tikzcd}$$

Depending upon the base and sometimes upon the conditions, the cleavage may be symmetric or asymmetric, as depicted above (see also p. 207 and Fig. 7). A preliminary study of the behaviour of B_4H_{10} with various Lewis bases revealed that the principal reaction is symmetric cleavage in which an adduct of B_3H_7 is formed.[301] Also it was apparent that the Lewis acid strength of B_3H_7 exceeds that of BH_3, because the co-ordinating ability (i.e. base strength) of the Lewis base can be correlated with the formation or non-formation of a BH_3 adduct. Accordingly the reaction may follow either of the alternative paths:[302, 303]

$$B_4H_{10}+2L \rightarrow L.B_3H_7+L.BH_3$$

or

$$2B_4H_{10}+2L \rightarrow 2L.B_3H_7+B_2H_6$$

Since bases containing trivalent nitrogen or phosphorus constitute the stronger Lewis bases, they preferentially react according to the former of the two equations. Ammonia, however, also cleaves tetraborane asymmetrically, rendering the situation complex, as is also the case with the diborane(6)-ammonia reaction discussed on pp. 111–112.

Tetraborane(10) was treated with an excess of ammonia at −70°C in Stock's laboratory and yielded a white involatile salt-like solid of apparent formula $B_4H_{10}.4NH_3$ that was readily soluble in liquid ammonia.[177] This product was not very stable and evolved ammonia and hydrogen in a vacuum at room temperature: on heating to 180°C it gave borazine $B_3N_3H_6$ in 40 % yield based on the equation

$$3B_4H_{10}.4NH_3 \rightarrow 4B_3N_3H_6+21H_2$$

On working with an excess of B_4H_{10}, ammonia gave an adduct that contained a smaller proportion of base and had a composition close to $B_4H_{10}.2\frac{1}{2}NH_3$, but this may have been a mixture. Electrolysis of B_4H_{10} in liquid ammonia solution yielded NH_3 and H_2 at the cathode and complex products at the anode.

The tetra-ammine of B_4H_{10} was a challenge to chemists for many years, and a number of exotic structures were suggested, such as $[NH_4]_2[(H_3B)_2NHBH_2NH_2BH_3]$.[304] Others, more perceptively, suggested that the substance might be a complicated mixture.[305] Clarification of the situation commenced with the investigations of Kodama, who was unable to obtain a single product of composition $B_4H_{10}.4NH_3$: however, a single substance of formula $B_4H_{10}.2NH_3$ was isolated from the reaction of NH_3 with B_4H_{10} in ether at −78°C.[306] On treatment with sodium in liquid ammonia, this compound gives NaB_3H_8 and boranamine (aminoborane)

$$B_4H_{10}.2NH_3+Na \xrightarrow[-78^\circ C]{NH_3} NaB_3H_8+BH_2NH_2+NH_3+\tfrac{1}{2}H_2$$

Alternatively, on treatment with HCl or HBr in ether at −78°C, the ammine salt $[BH_2(NH_3)_2]^+X^-$ [X=Cl, Br] and hydrogen are obtained. Also, excess of ammonia in ether at −78°C converts $B_4H_{10}.2NH_3$ to $B_3H_7.NH_3$.[307–10] The later results are more readily harmonized with a phase study of the system B_4H_{10}-NH_3, in which have been identified phases of composition $B_4H_{10}.2NH_3$, $B_4H_{10}.6NH_3$ and $B_4H_{10}.7NH_3$.[311] On the basis of the chemical evidence, it was concluded that, in analogy with the formulation of $B_2H_6.2NH_3$ as $[BH_2(NH_3)_2]^+BH_4^-$ considered on p. 111, $B_4H_{10}.2NH_3$ should be formulated as $[BH_2(NH_3)_2]^+[B_3H_8]^-$.[310] As in the case of diborane(6) (see p. 111 ff), it is evident that in the reaction of tetraborane(10) with ammonia both symmetric and asymmetric cleavage of the double bridge bond are possible. With amines, on the other hand, reaction seems to result in compounds of type $L.B_3H_7$,[308] and only the products of symmetric cleavage appear to have been observed. Nevertheless, it must be borne in mind that in other cases of apparently symmetric cleavage evidence exists for an initial asymmetric cleavage followed by a rapid hydride-ion transfer[312] (p. 169).

Metathetical reactions involving some of the above compounds have been carried out.[313] It was found that $[BH_2(NH_3)_2]^+BH_4^-$ reacts with NaB_3H_8 in ether at −78°C to give $[BH_2(NH_3)_2]^+[B_3H_8]^-$ and $NaBH_4$. At this temperature LiB_3H_8 reacts in the same way, but at 0°C there exists an equilibrium in which the starting materials $[BH_2(NH_3)_2]^+BH_4^-$ and LiB_3H_8 predominate. The structures of the two compounds $[BH_2(NH_3)_2]^+[B_3H_8]^-$ and $B_3H_7.NH_3$ have been investigated crystallographically.[314–16] The triborane fragments are depicted in the diagrams on pp. 167 and 172.

The reaction with trimethylamine is apparently different. Earlier workers[317, 318] passed B_4H_{10} into NMe_3 dissolved in tetrahydrofuran and obtained $H_3B.NMe_3$ and a poorly characterized compound, to which they assigned the formula $BH.xNMe_3$ [x=0·3–0·5], but which was probably impure $B_3H_7.NMe_3$. Other investigators report[301] that the B_3H_7 adduct is at first formed by simple symmetric cleavage, but that this in its turn is slowly cleaved by excess of the base to $BH_3.NMe_3$ plus a polymeric boron hydride: on the other hand, excess B_4H_{10} leads to other modes of decomposition with the appearance of B_2H_6, B_5H_9 and H_2, while the $BH_3.NMe_3$ is slowly converted to $B_3H_7.NMe_3$. Indeed, the reaction has been thought to be worth patenting.[319] The $B_3H_7.NMe_3$ is a white sublimable crystalline solid that is thermally stable up to 200°C and soluble in water and alcohol. More recently the unstable white solid adduct $B_4H_{10}.NMe_3$ has been reported to be the initial product of the reaction between B_4H_{10} and NMe_3 when it is carried out at a low enough temperature (−95°C).[320] On slow warming, the solid breaks down into diborane(6) and $B_3H_7.NMe_3$.

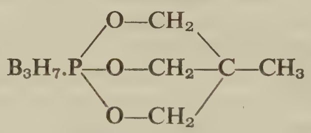
The reaction of B_4H_{10} with dimethylamine is basically different. The principal product of this reaction is μ-dimethylaminodiborane:[321]

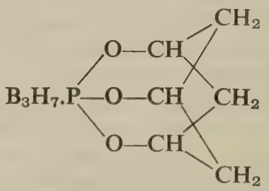
$$B_4H_{10} + 2NHMe_2 \rightarrow 2\mu\text{-}B_2H_5NMe_2 + H_2$$

Tetraborane(10) reacts with other classes of nitrogenous bases. From a reaction in which it was held with hydrazine in benzene at −23°C for 3 h in a sealed tube polymeric products of empirical formula $B_4H_9.xN_2H_4$ [x=1, 2, 3] that have a high calorific value were obtained.[322] The formula, if correct, would suggest that the product is either a mixture or is polymeric in nature. However, other workers report the formation of $B_4H_{10}.xN_2H_4$ [x=1, 2, 3] from the same reagents.[16] The evidence regarding the reaction of tetraborane(10) with pyridine is also not fully clarified. One report[318] states that if a mixture of B_4H_{10} and H_2 is bubbled through pyridine at 0°C, the products which can be isolated are $C_5H_5N.BH_3$ and $C_5H_5N.B_2H_4$. However, elsewhere[301] it is reported that the second product is $C_5H_5N.B_3H_7$, and that it is thermally stable though sensitive to atmospheric oxidation. The difference may be an outcome of different experimental procedures, since the action of excess base on $C_5H_5N.B_3H_7$ could produce $C_5H_5N.B_2H_4$ plus further $C_5H_5N.BH_3$.

With concentrated nitric acid B_4H_{10} reacts with explosive violence.[2]

On turning to the action with phosphorus compounds, it is seen that there is a need to investigate the behaviour of B_4H_{10} with phosphine. The reaction with trimethylphosphine to give $B_3H_7.PMe_3$ has been cited without experimental details;[33] however, at −95°C it has more recently been shown that the first product is the colourless solid adduct $B_4H_{10}.PMe_3$, which is converted on gradual warming in the absence of a solvent to $B_3H_7.PMe_3$ and B_2H_6.[320] In tetrahydrofuran B_4H_{10} reacts indirectly (*via* $B_3H_7.OC_4H_8$) with triphenylphosphine to form $B_3H_7.PPh_3$.[323] Phosphorus trifluoride is not a strong enough base to give a stable B_3H_7 adduct by direct reaction with B_4H_{10}, but both difluorophosphine PHF_2 and dimethylaminodifluorophosphine $P(NMe_2)F_2$ effect sequential cleavage to give not only $B_3H_7.PHF_2$ and $B_3H_7.P(NMe_2)F_2$, but also the diborane(4) adducts $B_2H_4.2PHF_2$ and $B_2H_4.2P(NMe_2)F_2$ respectively.[324, 325] These compounds, though not very stable, have definite melting points and reproducible vapour pressures at 0°C, and have been well characterized by ^{11}B and ^{31}P n.m.r. studies, as well as infrared spectroscopy. With PF_2X [$X=F$, Cl, Br] B_4H_{10} reacts directly to form $BH_3.PF_2X$ and $B_2H_4.2PF_2X$ complexes, but not more than traces of the $B_3H_7.PF_2X$ complex, which can notwithstanding be prepared in good yield from the dimethyl ether complex $B_3H_7.OMe_2$.[326] It appears that for the B_2H_4 adducts the boron-phosphorus stretching frequencies lie in the region 743–875 cm^{-1}. Tetraborane(10) also gives interesting B_3H_7 adducts with phosphite bases[327, 328] (cf. pp. 33–34):





For these compounds boron-phosphorus stretching frequencies have been located at 750–870 cm^{-1}.[329]

There are no reports of the behaviour of B_4H_{10} with compounds of arsenic or antimony.

REACTIONS WITH OXYGEN AND SULPHUR AND THEIR COMPOUNDS

Tetraborane(10) will burn in air, and its enthalpy of combustion to boric oxide according to the equation

$$B_4H_{10}(g)+5\tfrac{1}{2}O_2(g)\rightarrow 2B_2O_3(cryst.)+5H_2O(l)$$

is 965·8 kcal mol^{-1} as calculated from thermochemical data.[160, 330] The green colour imparted to the flame is due to the emission of the 'fluctuation' bands of vaporized boric oxide. Although, when pure, B_4H_{10} is not spontaneously inflammable, the flash point is nevertheless low: Stock and Massenez observed that explosions in contact with air were caused by the impure substance, that is, before it was freed from higher boranes and silanes. A useful review of the combustion properties of boranes[331] does not specifically deal with tetraborane, and supplies information concerning it only by inference. A separate account[332] of the reasons for the eventual collapse of the high-energy, boron-based fuel program in the United States is also relevant, in that tetraborane(10) was one of the compounds originally considered. In a study devoted specifically to the study of the explosive and partial oxidation of tetraborane(10),[333, 334] the explosions observed over a range of pressures and temperatures on heating B_4H_{10}-O_2 mixtures delineated a profile for the first explosion limit. The explosion region bounded by this limit is generally attributed to a branching chain reaction with chain initiation in the gas phase and chain breaking on the walls. The reaction is inhibited by tetraethyllead. In addition, a slow reaction is observed in the non-explosive region at lower temperatures in which, as discussed on p. 121 for the case of diborane(6), hydrogen and $H_2B_2O_3$ are among the products. This reaction is reported to follow the stoichiometric equation

$$B_4H_{10}+1\tfrac{1}{2}O_2\rightarrow B_2H_6+B_2H_2O_3+H_2$$

quite closely, except that varying amounts of the $H_2B_2O_3$ are split up into $B_2O_3+H_2$. Nevertheless, other workers[335] also observed the formation of a solid boron hydride and write the equation

$$B_4H_{10}+1\tfrac{1}{2}O_2\rightarrow \tfrac{1}{2}B_2H_6+\frac{1}{x}(BH)_x+2H_2+(1-\alpha)H_2B_2O_3+\alpha(H_2+B_2O_3)$$

Boroxine does not appear, as confirmed by a mass-spectrometric study.[335] Borane peroxide $H_3B.O_2$ is however apparently formed as an intermediate, and this is considered to be the precursor of $H_2B_2O_3$.[335, 336]

The observed liberation of hydrogen in the partial oxidation of B_4H_{10}[333, 334] reflects the higher affinity for oxygen possessed by boron over that possessed by hydrogen. It follows that B_4H_{10} is a strong reducing agent, but though it has been observed to reduce $KMnO_4$ to MnO_2 and to react explosively with concentrated nitric acid,[2] this aspect of its chemistry has been little studied. Nevertheless it is considered to be a stronger reducing agent than B_2H_6,[337] whose powers in this respect are much better known (p. 99).

Stock and Massenez found that, unlike diborane(6), which is immediately hydrolyzed by water, tetraborane(10) hydrolyzes only slowly.[1] The overall equation is

$$B_4H_{10}+12H_2O \rightarrow 4H_3BO_3+11H_2$$

One sample of B_4H_{10}, which was allowed to stand with water over mercury at room temperature, underwent a 50 % decomposition in 2 h and almost complete destruction in 24 h. To what extent this hydrolysis depends on prior thermal decomposition has not been established. Tetraborane(10) is almost immiscible with water, but the hydrolysis can be accelerated by warming and shaking the mixture. The slowness of the hydrolysis reaction was an essential factor in the original preparative methods for the boron hydrides,[2] because the reaction with dilute hydrochloric acid is no faster.

With solid alkali metal hydroxides or their concentrated aqueous solutions B_4H_{10} forms a product which is stable in the dry state, and which was originally thought to be a hypoborate.[244] If the product with KOH is heated to 500°C metallic potassium distils off. Solutions of these supposed hypoborates are now known to contain mainly tetrahydroborates and are strongly reducing,[245] characteristically reducing solutions of nickel salts to nickel boride: on acidification, such solutions decompose immediately with the formation of boric acid and hydrogen.

Stock and Massenez also found that tetraborane(10) undergoes alcoholysis with ethanol, evolving about eight times its volume of hydrogen in an exothermic reaction and forming a liquid with a pungent, disgusting odour.[1] When water is added to this liquid, the remainder of the hydridic hydrogen is discharged. Burg and Stone found that at -78°C tetraborane(10) reacts with ethanol to form H_2, $B(OEt)_3$, $BH(OEt)_2$ and a polymeric material containing boron and ethoxy groups.[317] The molar ratio of boron in these boron products is approximately 4:3:1. One $BD(OEt)_2$ molecule is formed to every two $BH(OEt)_2$ molecules in the reaction of B_4H_{10} with EtOD: the diethoxydeuteroborane is thought to be formed during the initial breaking of the B—B bond, when, apparently, the ethoxy group becomes attached to one boron atom and the deuterium to the other.[338]

Alcoholysis is much more rapid in the presence of iodine, which causes it to go to completion with excess methanol even at room temperature.[339, 340] The principal equation is possibly to be written

$$B_4H_{10}+9I_2+18MeOH \xrightarrow[25°C]{MeOH} 18MeI+4H_3BO_3+6H_2O+2H_2$$

Except for the hydrogen, the reaction products were unfortunately not determined, and the original assumption that the iodine appears as hydrogen iodide[340] is a most unlikely one: in similar reactions with iodine and an alcohol or ether, both B_2H_6 and B_5H_9 give the alkyl iodide without a trace of hydrogen iodide,[341] and it is not likely that B_4H_{10} behaves differently.

There is abundant evidence that tetraborane(10) is at its most versatile as a reagent when dissolved in ether.[342] In a preliminary study of the reactions of B_4H_{10} with ethers, it was found that the principal reaction is a symmetric cleavage in which adducts of the strong Lewis acid B_3H_7 are formed. Such adducts readily undergo substitution with stronger bases.[309] The B_3H_7 complexes of Et_2O, of tetrahydrofuran and of ethyleneglycol ethers have been obtained,[301] although ethers are weaker Lewis bases than, for example, amines. For this reason they give rise to less stable B_3H_7 derivatives, depending on the coordinating ability of the ether. Thus the tetrahydrofuran adduct $B_3H_7.OC_4H_8$

is a white crystalline solid melting without decomposition at 39°C, and $B_3H_7.OEt_2$ is an involatile liquid which decomposes at room temperature with the formation of pentaborane(9) and diborane, while evidence for the formation of a corresponding diphenyl ether adduct is not good.[301] The tetrahydrofuran complex was found to react smoothly with amines to give the corresponding amine adduct, and this is a convenient way of preparing the latter free from the corresponding BH_3.amine complex. The behaviour of B_4H_{10} with dimethyl ether has also been investigated.[343] The adduct $B_3H_7.OMe_2$ is prepared by the room-temperature reaction of B_4H_{10} with Me_2O for 5 min. It decomposes in 1 h at room temperature to dimethyl ether and a mixture of boron hydrides.

Asymmetric cleavage of B_4H_{10} in ethers has also been observed: it has already been noted (p. 171) that the preparation of NaB_3H_8 from B_4H_{10} is facilitated by the use of ethers as solvents.[296] Evidence from ^{11}B n.m.r. studies suggests that asymmetric cleavage of B_4H_{10} occurs in solutions in ethers such as tetrahydrofuran, tetrahydropyran and diglyme,[312] each of which acts as a Lewis base (L):

$$B_4H_{10}+2L \rightarrow [BH_2L_2]^+[B_3H_8]^-$$

When μ-B_4H_9D is allowed to react with monoglyme at room temperature and the octahydrotriborate(1−) anion produced is subsequently isolated by the addition of a quaternary ammonium salt, the product contains one deuterium atom per molecule. This indicates an asymmetric cleavage mechanism, because symmetric cleavage would necessarily involve a 25 % loss of deuterium.[344] It is therefore clear that, as in its reactions with NH_3, both symmetric and asymmetric cleavage are facile processes for B_4H_{10} dissolved in ethers of high basicity.

How tetraborane(10) behaves towards elementary sulphur, selenium and tellurium has not been investigated. Although the reactions of B_4H_{10} with sulphur compounds have received but scant attention, it would appear from the formation of B_3H_7 adducts with SMe_2 and thiophen respectively[301] that Lewis bases containing sulphur effect symmetric cleavage of the borane. Nothing is known concerning the reactions of B_4H_{10} with compounds of selenium and tellurium.

REACTIONS WITH HALOGENS AND THEIR COMPOUNDS

Because fluorine and chlorine react too violently with boranes while the reaction of iodine is too sluggish, the only reaction of tetraborane(10) with a halogen to have received study is that with bromine. With the B_4H_{10} in excess under controlled conditions at −15°C, the liquid product 2-B_4H_9Br is obtained.[276, 278] Properties of the compound are described on p. 212. No investigations using a larger proportion of bromine have been reported, and it is not known whether B_4H_{10} can be more heavily brominated. In the presence of methanol, iodine breaks down tetraborane(10) completely, as noted on p. 217.

Tetraborane(10) reacts sluggishly with hydrogen chloride, as discussed on p. 212. In its behaviour with halogenophosphines (p. 216), reactions involving the halogen ligands are not among those found. Otherwise little is known about the behaviour of B_4H_{10} towards halogen compounds.

REACTIONS FORMING CARBORANES

Carboranes form the subject of a separate section on p. 450 of this book, but the role of tetraborane(10) in their formation requires a brief summary here. It is clear from a close reading of the work carried out by Stock and his collaborators[2] that some of the interesting unidentified products containing B, C and H which they obtained from B_4H_{10} reactions were probably carborane mixtures. Although in general the reaction of pentaborane(9) with acetylenes was later to become the preferred route to *nido*- and *closo*-carboranes of lower molecular weight, a number of syntheses involving B_4H_{10} have been established.[345]

Methyl derivatives of *nido*-2,3,6-$C_3B_3H_7$ have been obtained from the slow reaction of acetylene with B_4H_{10} at room temperature; these were identified as the 3-methyl, 2,3-dimethyl and 3,6-dimethyl derivatives.[346] It is necessary to note that the conventional numbering system used in this account often differs from that used by the original authors (in this case 2,3,4-$C_3B_3H_7$): this revision is explained on p. 451. Additionally, it should be noted that optical isomers of formula $C_3B_3H_6X$ are obtained by substitution at the carbon atoms numbered 3 or 6, a point which may be clarified by reference to the structure of 3-$C_3B_3H_6Me$ depicted in Fig. 9: such enantiomers have so far only been resolved for certain nearly icosahedral higher carboranes. The products obtained by Bramlett and Grimes[346] would be more precisely described by the formulae 3(6)-$C_3B_3H_6Me$, 2,3(6)-$C_3B_3H_5Me_2$ and 3,6-$C_3B_3H_5Me_2$, but, for simplicity, we shall not distinguish enantiomeric forms in this section. The same workers also carried out a flash reaction of B_4H_{10} with acetylene at 100°C, when they obtained a series of *closo*-carborane products.[347] By combined gas-chromatographic and spectroscopic techniques, these products were identified (with their yields) as 2-$C_2B_3H_4Me$ (4 %), 1,6-$C_2B_4H_6$ (4 %), $C_2B_5H_7$ (35 %), 1-$C_2B_5H_6Me$ (9 %), 2-$C_2B_5H_6Me$ (17 %), 3-$C_2B_5H_6Me$ (9 %), 5-$C_2B_5H_6Me$ (4 %), $C_2B_8H_{10}$ (11 %) and *B*-Me-$C_2B_8H_9$ (7 %). The room-temperature reaction was extended to methylacetylene and dimethylacetylene by the same group.[348, 349] From dimethylacetylene they obtained 4,5-$C_2Me_2B_4H_6$ as the only volatile product, but from methylacetylene they obtained 4-$C_2B_4H_7Me$, 2-CB_5H_8Me, two *C,B*-Me_2-CB_5H_7 isomers and 3-Et-2,6-Me_2-$C_3B_3H_4$ as products.[349] When they carried out flash reactions with the methyl-substituted acetylenes and B_4H_{10}, they obtained *closo*-carborane products almost exclusively, apart from traces of alkenes. The species $C_2B_3H_5$, 2-$C_2B_3H_4Me$, *B,C*-$C_2B_3H_3Me_2$ and $C_2B_5H_7$ are prominent products in both reactions, but a large number of other derivatives are also obtained. Both 2-$C_2B_5H_6Me$ and 1,7-$C_2B_5H_5Me_2$ are obtained in good yield from methylacetylene, while 1-$C_2B_5H_6Et$ is correspondingly obtained from C_2Me_2.[350] Recently, Franz and Grimes have studied the mechanism of the room-temperature reaction of B_4H_{10} with C_2H_2 with the aid of deuterium-labelling techniques.[351] C_2D_2 and B_4H_{10} give only C-deuterated products.[352, 353]

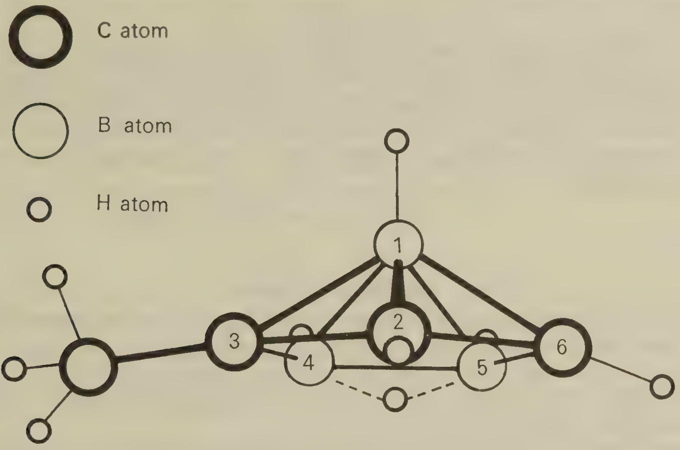


FIG. 9.—Basic structure of 3-methyl-*nido*-2,3,6-tricarbahexaborane(7) $C_3B_3H_6Me$. Numbered light circles represent boron atoms, numbered heavy circles carbon atoms, small circles hydrogen atoms

Reaction Mechanisms

PYROLYSIS

As one of the less stable isolable boranes, B_4H_{10} is readily pyrolyzed just above room temperature[258, 259, 267] (and indeed decomposes slowly without heating). The principal products are initially B_2H_6, B_5H_{11}, B_5H_9 and H_2, the B_5H_{11} preceding or largely preceding the B_5H_9. With the passage of time, higher boranes, especially $B_{10}H_{14}$, are also formed, and the ultimate products are essentially the same as those observed in the exhaustive pyrolysis of B_2H_6 (p. 79). Indeed, B_4H_{10} is the first isolable intermediate in the pyrolysis of B_2H_6.[81]

Although other schemes had tentatively been suggested, there is now no reason to doubt[81] that the initial act of decomposition is to produce the non-isolable fragment B_3H_7:

$$B_4H_{10} \rightarrow B_3H_7 + BH_3$$

That this step occurs and is reversible under mild enough conditions, finds support in the observation that B_4H_{10} exchanges BH_3 for BD_3 with B_2D_6:[85, 253] and since B_4H_{10} is methylated by B_2H_5Me or 1,2-$B_2H_4Me_2$,[273] the exchange of BH_3 for BH_2Me is also implied. Further support for B_3H_7 formation arises from the observation that H_2 slowly converts B_4H_{10} to B_2H_6,[221] which is most simply explained[81] by the following reaction sequence:

$$B_3H_7 + H_2 \rightarrow B_3H_9$$

followed by

$$2B_3H_9 \rightarrow 3B_2H_6$$

Added hydrogen not only retards the pyrolysis of B_4H_{10}, but also increases the relative proportion of B_4H_{10} that is converted to B_2H_6 plus B_5H_{11}.[259] This suggests that B_3H_7 is not only instrumental in furthering the decomposition of B_4H_{10}, but is largely responsible for the formation of other products, the proportion of which can be reduced by depressing the B_3H_7 concentration.

But since no deuterium exchange was observed between D_2 and B_4H_{10} during 130 min at 45°C,[85, 253] the alternative equilibrium once assumed, namely

$$B_4H_{10} \rightleftharpoons B_4H_8 + H_2$$

is of no significance, at least, for the lower temperature range normally employed in pyrolysis studies. True, with a much higher D_2:B_4H_{10} ratio of about 12:1 evidence was found for the presence of deuterium in the residual B_4H_{10} after 135 min at 45°C,[263] but, as pointed out by the investigator, the results are not meaningful because appreciable quantities of diborane(6) were simultaneously formed, which compound undergoes ready exchange with both deuterium and tetraborane(10). In any case, with the increased deuterium the significance of the reversible reaction cited on p. 177

$$B_3H_7 + H_2 \rightleftharpoons B_3H_9$$

is enhanced, which could lead to the formation of deuterated B_2H_6 and deuterated B_4H_{10} without invoking the species B_4H_8.

The experimental order of reaction for the pyrolysis of B_4H_{10} is apparently not very constant, the observed values varying between 1 and 1·5 according to the conditions. Pearson and Edwards[259] observed an order of unity over the temperature range 60–100°C, and Morrey and Hill[258] tacitly concur with this; but Bond and Pinsky,[267] who worked at 40–60°C, while agreeing that at 60°C the order approaches unity as the pressure is lowered, found that at higher pressures and at lower temperatures the observed order approximates to 1·5. The order of unity is readily explicable, but—otherwise than in the case of diborane(6)—no likely mechanism can be devised for B_4H_{10} which would result in a reaction order of 1·5. An assumed mechanism involving BH_2[267] is thermodynamically unlikely and is at variance with all other known facts concerning borane interconversion mechanisms.[81] Another possibility, that a competing bimolecular reaction such as

$$2B_4H_{10} \rightarrow B_2H_6 + 2B_3H_7$$

might become important (relatively speaking) at higher pressures and lower temperatures, cannot be ruled out completely, but it would nevertheless be a rare case of an isolable hydrogen-rich borane reacting with itself. A much more likely explanation of the apparent departure from first-order kinetics under certain conditions is the inhibiting action of the H_2 which accumulates during the pyrolysis.

Separate experiments with added hydrogen carried out by the earlier workers[259] showed that hydrogen substantially inhibits, but does not fully prevent, B_4H_{10} decomposition. Since H_2 is produced during the pyrolysis of B_4H_{10} alone, such a complication means that the curve showing the change with time in the concentration of B_4H_{10} would show a greater progressive flattening than would accord with first-order kinetics, and the result would be an apparent order higher than unity.[267]

There is thus justification, at least as far as the principal mechanism is concerned, for accepting that the true order for pyrolysis of B_4H_{10} in the absence of hydrogen is indeed unity, as it is for B_4H_{10} in isotope-exchange experiments with $^{10}B_2D_6$.[84, 85] And since all subsequent steps involved in the production of B_2H_6 and B_5H_{11} in the B_4H_{10} pyrolysis are bimolecular and are relatively fast, the original B_3H_7-producing unimolecular step given above will be rate-determining, as is also the case in the isotope-exchange studies.[85]

Both fragments thereby produced, i.e. BH_3 and B_3H_7, can reform B_4H_{10}; but since this does not effect decomposition, some fragments must react in other ways. The reaction of BH_3 with further tetraborane(10)

$$BH_3 + B_4H_{10} \rightarrow B_5H_{11} + H_2$$

would be expected to occur and to be exothermic, not only because one isolable and one non-isolable reactants give two isolable products, but also because the reaction

$$B_2H_6 + 2B_4H_{10} \rightleftharpoons 2B_5H_{11} + 2H_2$$

can be made to proceed in either direction.[221] Though it is now clear[81] that in neither direction can it be said to occur in a single step as written, rate constants have been determined for the forward reaction from a kinetic investigation,[249] while the enthalpy of reaction has been calculated at 7·56 kcal mol^{-1} from equilibrium studies[202] and amounts to 9·3 kcal mol^{-1} if derived directly from thermochemical data.[160] From *a priori* considerations the latter value is probably to be preferred, especially if it is borne in mind that the reversible reaction is at best only a *pseudo*-equilibrium, and is accompanied by other reactions leading to different products.[249] Although the forward reaction with B_2H_6 is thus mildly endothermic, allowance for the dissociation energy $D(H_3B \cdots BH_3)$ means that the reaction of B_4H_{10} with BH_3 is decidedly exothermic, even though a precise value cannot be set to the heat of reaction because of uncertainty in the bridge-bond dissociation energy of diborane(6).

Likewise the reaction of B_4H_{10} with B_3H_7

$$B_3H_7 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11}$$

would be expected to be exothermic, since again two isolable products are formed, while the high reactivity of the reactants would make its occurrence likely. That it occurs is indicated by the presence of large amounts of B_2H_6 among the initial pyrolysis products of B_4H_{10}, as shown graphically in Fig. 10, which presents data observed by Pearson and Edwards and reported by Morrey and Hill.[258] (The latter workers made observations that were in essential respects similar, except that, apparently because they used a brass cell instead of a glass vessel, B_5H_9 was observed in place of B_5H_{11}.) A combination of the reactions of BH_3 and B_3H_7 respectively with B_4H_{10} provides a good explanation of the initial pyrolysis products, since they add up to the overall material balance

$$3B_4H_{10} = B_2H_6 + 2B_5H_{11} + H_2$$

But close inspection of Fig. 10 reveals that in the earliest stages B_5H_{11}, notwithstanding the fact that it too is decomposing, is being formed at more than twice the rate of B_2H_6. This appears to demand the formation of additional B_5H_{11} from the interaction of B_3H_7 fragments with themselves, which at the comparatively low temperatures of B_4H_{10} pyrolysis will preferably react by condensation and initiate the following sequence of reactions:

$$2B_3H_7 \rightarrow B_6H_{12} + H_2$$
$$B_3H_7 + B_6H_{12} \rightarrow B_4H_8 + B_5H_{11}$$
$$BH_3 + B_4H_8 \rightarrow B_5H_{11}$$

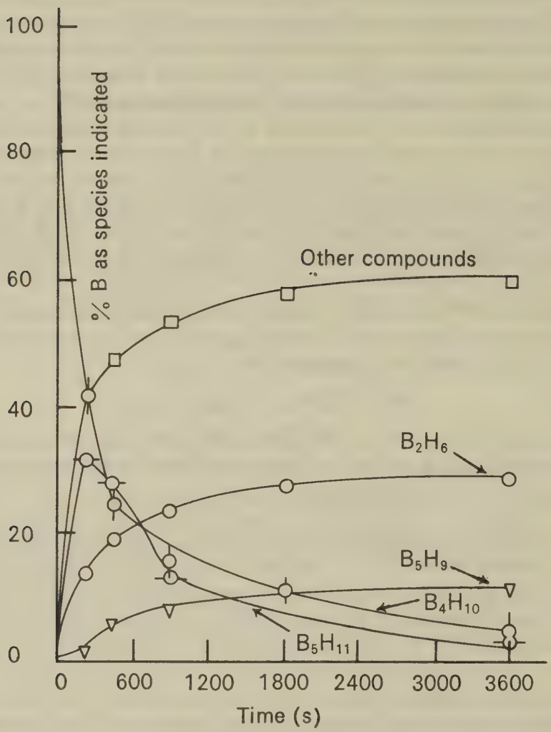


FIG. 10.—Progressive pyrolysis of B_4H_{10} at 100°C and initial pressure 4·55 Torr, showing changes in concentration of the products as plotted by Morrey and Hill (Ref. 258) from unpublished data of Pearson and Edwards (cf. Ref. 259)

Not only has B_6H_{12}, along with higher boranes, been observed in the pyrolysis of B_4H_{10},[244, 259, 263] but also traces of B_4H_8 have been identified in the mass spectrograph.[354] But the interaction of BH_3 molecules among themselves is initially hindered by a considerable energy barrier, for which there is other evidence.[214, 81] However, BH_3 reacts with B_4H_{10} to liberate H_2, and once significant quantities of diborane(6) have been formed from B_4H_{10} *via* B_3H_7 and B_3H_9 by reactions mentioned above, BH_3 can in part give rise to further B_2H_6 by an energetically favourable sequence:

$$BH_3 + B_2H_6 \rightarrow B_3H_9$$

followed by

$$2B_3H_9 \rightarrow 3B_2H_6$$

(B_3H_9 can however also react as $B_2H_6 + BH_3$ with B_4H_{10}—p. 136). On the other hand, the accumulation of H_2 will lead to a progressively faster decomposition of B_5H_{11}, since the reaction

$$B_5H_{11} + H_2 \rightarrow B_4H_{10} + BH_3$$

becomes important. These effects account readily for the progressive increase in the concentration of B_2H_6 at the expense of B_5H_{11} and the subsequent crossing of the B_2H_6 and B_5H_{11} concentration curves. The formation of small quantities of B_5H_9 is explicable by the decomposition of a part of the B_6H_{12} formed from the condensation of B_3H_7 as suggested above, the steps being:

$$2B_3H_7 \rightarrow B_6H_{12} + H_2$$

$$B_6H_{12} \rightarrow B_5H_9 + BH_3$$

But at later stages larger quantities of B_5H_9 are produced in other ways, because with the decomposition of the majority of the B_4H_{10} the situation with respect to the products becomes progressively more like that observed in the pyrolysis of diborane(6),[81] while the accumulation of B_2H_6 will mean that the pyrolysis mechanism already discussed for this compound (p. 136) will eventually take over. The pyrolysis mechanism of B_4H_{10} can therefore, without straining the evidence, be explained in a self-consistent and satisfactory way that is in excellent agreement with observation.

CO-PYROLYSIS WITH DIBORANE(6)

Experiments on the co-pyrolysis of B_4H_{10} and B_2H_6[259, 249] have unambiguously shown that both species are consumed simultaneously, the main products being B_5H_{11} and H_2. The mechanism is thus different from that of the pyrolysis of either species on its own. Indeed, the rapid consumption of B_2H_6 occurs at a temperature where its pyrolysis is normally slow or insignificant.

The B_4H_{10} is consumed twice as fast as the B_2H_6 over a wide range of conditions. The rate at which both species disappear is directly proportional to the pressure of B_4H_{10}, but independent of the pressure of B_2H_6; that is to say, the co-pyrolysis kinetics are first order in $[B_4H_{10}]$ but zero order in $[B_2H_6]$. The rate-controlling step will therefore be the same dissociation of B_4H_{10} into $B_3H_7 + BH_3$ that was proposed on p. 220 for the pyrolysis of B_4H_{10} alone. This is also concordant with the results of isotope-exchange studies.[85, 253] The ambient concentrations of BH_3 and B_3H_7 will however be reduced by the presence of large amounts of B_2H_6, which can react with either fragment. This accounts for the consumption of B_2H_6. As described on p. 177 the BH_3 will immediately react by a very fast reaction with B_2H_6 to produce B_3H_9. This species cannot react with more B_2H_6 (except to exchange BH_3 groups), but can react as though it were $B_2H_6 + BH_3$ with the other species present in high concentration, namely B_4H_{10}, according to the equation

$$B_3H_9 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11} + H_2$$

This is presumably an exothermic reaction, as all the products are sufficiently stable to be isolated, which is not true of the reactant B_3H_9.

The other fragment initially produced, B_3H_7, can react with B_4H_{10} in the manner described on p. 221, or, alternatively, with B_2H_6 to produce a second BH_3 molecule

$$B_3H_7 + B_2H_6 \rightarrow B_4H_{10} + BH_3$$

This step has a low activation energy because it has been observed at 0°C,[95] and it is also an essential step in the production of isotopically labelled tetraborane from $Na^{10}B_3H_8$ and B_2H_6[250]

$${}^{10}B_3H_7 + {}^{11}B_2H_6 \rightarrow {}^{10}B_3{}^{11}BH_{10} + {}^{11}BH_3$$

The second BH_3 molecule will react as before. Hence, if the relevant equations are accordingly given double weight, the net effect resulting from the initial act of decomposition is given by the following sum:

$$\begin{aligned} B_4H_{10} &\rightarrow B_3H_7 + BH_3 \\ B_3H_7 + B_2H_6 &\rightarrow B_4H_{10} + BH_3 \\ 2BH_3 + 2B_2H_6 &\rightarrow 2B_3H_9 \\ \underline{2B_3H_9 + 2B_4H_{10}} &\underline{\rightarrow 2B_2H_6 + 2B_5H_{11} + 2H_2} \\ \text{giving} \quad 2B_4H_{10} + B_2H_6 &= 2B_5H_{11} + 2H_2 \end{aligned}$$

The overall equation is in excellent agreement with the observed material balance.[259, 221, 249] It is clear that over the range of conditions studied the B_2H_6 competes very effectively with the B_4H_{10} for the removal of B_3H_7, for this stoichiometry would otherwise not have resulted. It is immaterial, however, for the overall material balance if some of the B_3H_9 disappears by the reaction $2B_3H_9 \rightarrow 3B_2H_6$, because it is readily seen that substituting this step for the fourth step above leads to a situation of complex equilibrium in which no net decomposition occurs. Neither does it make any difference to the material balance if the third and fourth steps above are partly replaced by the step

$$2BH_3+2B_4H_{10} \rightarrow 2B_5H_{11}+2H_2$$

Thus, since the total change is effected by the spontaneous dissociation of a single B_4H_{10} molecule, the kinetics of the co-pyrolysis are seen to be mechanistically explained in a natural and satisfying manner that renders the assumption of the decomposition $B_4H_{10} \rightarrow B_4H_8+H_2$ as a competing initial step completely unnecessary.

ISOTOPE-EXCHANGE WITH DIBORANE(6)

The B_4H_{10}-B_2D_6 isotope-exchange reaction has been studied in some detail over the temperature range 25–45°C, but only brief reference was made to experiments involving $^{10}B_2D_6$.[84] Both hydrogen and boron exchange readily, with a reported H:B exchange ratio of >3.[85] Molecular D_2 was however found to undergo no exchange with B_4H_{10} at 45°C.[85, 253] All the evidence therefore points to exchange taking place *via* BH_3 groups, and to the fact that a secondary factor (e.g. an isotope effect) could explain why the H:B ratio is not precisely 3.

But there is a more important complication. The order of the reaction is unity with respect to $[B_4H_{10}]$, but fractional with respect to $[B_2H_6]$; moreover, the usual logarithmic plot of the rate versus time is not linear, but shows a pronounced curvature that becomes evident after a comparatively short time. This has been explained as the result of two simultaneous mechanisms, each with its own rate-controlling step.[84, 85] The most recent results imply that the faster mechanism leads to the formation of 2,4-$B_4H_8D_2$.[256] Attempts to resolve the composite curve into its two components by the standard procedure were accomplished with difficulty for the stated reason that the precision of measurement becomes rather poor as the reaction proceeds;[84] but, after resolution, the two components were found to correspond to orders of approximately 0·5 and 0·25 respectively in $[B_2D_6]$, both being of order 1 with respect to $[B_4H_{10}]$. The associated activation energies are 14·1 and 25·5 kcal mol^{-1} respectively, so that the relative rates would change with temperature, having a ratio of unity at 25°C. The mechanism suggested by the original workers[84] in an attempt to explain this peculiar result is unsatisfactory, not least because it includes the assumed step

$$^{10}BD_3+B_4H_{10} \rightarrow {}^{10}BD_3B_3H_7+BH_3$$

whereas BH_3 is now known[81] to react exothermically with B_4H_{10} in a totally different manner, i.e.:

$$BH_3+B_4H_{10} \rightarrow B_5H_{11}+H_2$$

The later suggestion of Koski,[85] that the mechanism is based on a dissociation of B_4H_{10} into two fragments, probably

$$B_4H_{10} \rightarrow B_3H_7+BH_3$$

is however satisfactory, and harmonizes with present knowledge of the pyrolysis of B_4H_{10} and its copyrolysis with diborane(6), as presented on pp. 219 and 223.

A further complication is caused by the competing spontaneous decomposition of B_4H_{10} at the temperature of the experiment. The earlier investigators believed this could be dismissed,[84] but the most recent work[267] has clearly shown that pyrolysis of tetraborane(10) is significant in 1 h at 40°C. This is serious, because hydrogen is one of the products, and this reacts with both B_5H_{11}, which is also produced, and indirectly with B_4H_{10}. The measurements would become increasingly displaced relative to those to be expected from the exchange mechanism alone, and this could invalidate the sensitive procedure adopted for unravelling the components of the composite isotope-exchange curve. Particularly because no likely mechanisms can be readily devised to explain reaction orders of 0·25 and 0·5 in $[B_2D_6]$, it is more likely that the overall fractional order with respect to B_2D_6 is to be explained by a simultaneous occurrence of a zero-order and first-order decomposition step.

The zero-order decomposition is the faster in the higher temperature region, and the reaction order is readily explained by the following mechanism, which harmonizes with what has already been concluded for the B_4H_{10}-B_2H_6 copyrolysis:

$$B_4H_{10} \rightarrow B_3H_7 + BH_3 \text{ (rate-controlling)}$$
$$B_3H_7 + B_2D_6 \rightarrow B_4H_7D_3 + BD_3$$
$$BH_3 + B_2D_6 \rightarrow B_3H_3D_6$$
$$BD_3 + B_2D_6 \rightarrow B_3D_9$$
$$B_3H_3D_6 + B_3D_9 \rightarrow B_2H_3D_3 + 2B_2D_6$$

The net change then becomes

$$B_4H_{10} + B_2D_6 = B_4H_7D_3 + B_2H_3D_3$$

Such a mechanism is first order in $[B_4H_{10}]$ and zero order in $[B_2D_6]$, and since some of the steps are reversible, a departure from precisely 3 for the H:B exchange ratio is readily explicable. The change in order and mechanism means that the activation energy is in need of revision, but will still be near 25·5 kcal mol.$^{-1}$

The component which is first order in $[B_2D_6]$ can readily be written as the rate-controlling step

$$B_2D_6 + B_4H_{10} \rightarrow B_3H_3D_6 + B_3H_7$$

This step would absorb less energy than the unimolecular dissociation of B_4H_{10}, so that a lower activation energy is not surprising. In its subsequent steps the exchange reaction could proceed as before, the resultant net equation remaining the same. A rational explanation of the mechanism of exchange is thus forthcoming, but further experimental study is desirable.

OTHER REACTIONS

For other reactions involving tetraborane(10), mechanistic or kinetic data are available in only a very few cases. Thus the pyrolysis of B_4H_{10} in the presence of carbon monoxide leads to the formation of some tetraborane(8) carbonyl,[78] and this has been studied kinetically.[355, 96]

$$B_4H_{10} + CO \rightarrow B_4H_8CO + H_2$$

Over the range 80–110°C the activation energy was measured as 24·6 kcal mol^{-1} and the pre-exponential factor as $1{\cdot}12 \times 10^{14}$. The reaction is moreover first order with respect to $[B_4H_{10}]$, but zero order with respect to [CO]. At first sight this would appear to indicate that the rate-controlling step is the unimolecular elimination of H_2 from B_4H_{10}, and that this is followed by the addition of the residual B_4H_8 to carbon monoxide. However, although B_4H_{10} can be induced to decompose partly in this manner under the conditions of the mass spectrometer,[47, 82] it is unlikely to be a major step in the present reaction, as other evidence shows. Firstly we have seen that under mild conditions B_4H_{10} preferentially decomposes into $B_3H_7 + BH_3$. Secondly it will not undergo deuterium exchange with D_2 at 45°C.[85] True, this does not rigidly exclude the possibility above 80°C, but an alternative sequence is:

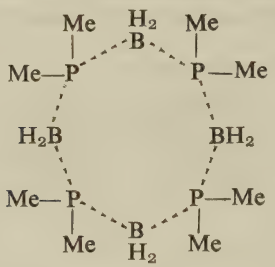
$$B_4H_{10} \rightarrow B_3H_7 + BH_3 \text{ (rate-controlling)}$$
$$BH_3 + CO \rightarrow BH_3CO$$
$$BH_3CO + B_3H_7 \rightarrow B_4H_8CO + H_2$$

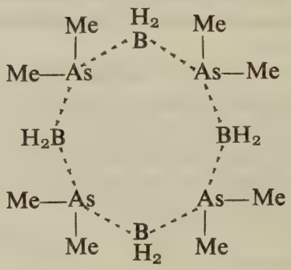
This mechanism involves the same rate-controlling step as the co-pyrolysis and isotope-exchange mechanisms of $B_4H_{10}$with B_2H_6, and it is to be noted that the experimental activation energies are strikingly similar.

A quite different type of mechanism arises in the reaction of B_4H_{10} with sodium tetrahydroborate, and this has been partly elucidated by isotope studies. When B_4H_{10} and $NaBD_4$ are reacted in diglyme at -45°C, the final products are NaB_3H_7D and a mixture of deuterated diborane(6) molecules of average composition $B_2H_3D_3$.[356] This seems to indicate quite clearly that, in the presence of the ether, a BH_3 group is split from the B_4H_{10} molecule to leave a B_3H_7 fragment, and that a deuteride ion D^- is transferred to the B_3H_7 from the BD_4^- ion in solution, so producing a monodeutero-octahydrotriborate(1−) ion. But when μ-B_4H_9D in monoglyme was converted by the addition of a tetraalkylammonium chloride into an octahydrotriborate(1 −), the product was found to contain one deuterium atom per $B_3H_8^-$ ion, showing that in this case an asymmetric cleavage of μ-B_4H_9D occurs.[344]

TETRABORANE(12), B_4H_{12}

Neither B_4H_{12} nor any other neutral tetraborane containing more hydrogen than tetraborane(10) is known. A structure homologous with that proposed for the transitory species B_3H_9 (p. 177) and consisting of a ring of four BH_2 groups linked by bridging hydrogen atoms is conceivable, but the lack of evidence for even a transitory species of formula B_4H_{12} is not unlikely to be connected with a thermodynamic instability with respect to $2B_2H_6$. However, μ-substituted derivatives of surprising thermodynamic and chemical stability are known in the solid tetramers of dimethylphosphinoborane (m.p. 161°C)[357] and dimethylarsinoborane (m.p. 150°C)[358] described on p. 118, which





are prepared along with the trimers by heating B_2H_6 with $PHMe_2$ and $AsHMe_2$ respectively. The phosphinoborane (tetramer plus trimer) is also prepared by heating the bis-borane adduct of tetramethyldiphosphine,[359]

$$nP_2Me_4.2BH_3 \xrightarrow{220^\circ C} 2(Me_2PBH_2)_n + nH_2$$

In the phosphorus compound, the 8-membered ring is puckered,[360] and presumably this is also true of the arsenic compound: the P—B interatomic distance (2·08 Å) is much greater than the P—C single-bond distance (1·84 Å)[360] and is compatible with a fractional bond order. The P—B stretching frequencies occur within the range 500–700 cm^{-1} [361] and are also distinctly low. The PBP angle is 104 ± 2° and the BPB angle 125 ± 1°.[360] Other B_4H_{12} derivatives of a similar nature are known, including the bis(trifluoromethyl)phosphinoborane tetramer $(H_2BP(CF_3)_2)_4$ (m.p. 116°C).[362]

An interesting long-lived gaseous intermediate of molecular weight close to 72 and apparent formula $B_4H_{12}O$ has been isolated in experiments on the oxidation of pentaborane(9).[363, 364] It is unstable, and the structure is unknown. Although, formally, it may appear to be a possible oxygen adduct of an unknown tetraborane(12), such evidence as exists makes this appear doubtful. Its spectrum[364] contains a band at 1390 cm^{-1} corresponding to the B—O linkage, but is otherwise exceedingly simple for a species containing 17 atoms, indicating that the molecule must be highly symmetrical. Moreover, the same intermediate has been detected in diborane(6)-oxygen mixtures that are undergoing reaction while heated to near the third thermal explosion limit. The compound gives boric acid with water without requiring further elementary oxygen. Clearly it merits further study.

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SECTION B5

THE HIGHER BORANES AND THEIR DERIVATIVES

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(*Manuscript received 15 September, 1970*)

PART 1: INTRODUCTION

The field of boron hydride chemistry has advanced remarkably since it was treated in Mellor in 1924. The apparent anomalies in the molecular constitution of these compounds have now been resolved by the application of modern techniques of structure determination and their structures have been rationalized in terms of modern bonding theory.

This Section deals with those boron hydrides having more than four boron atoms in their molecules, and their derivatives. Nineteen such neutral molecular boranes have been definitely characterized (in addition to B_2H_6 and B_4H_{10}, mentioned in the preceding Section B4). These are: B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{12}, B_8H_{14}, B_8H_{16}, B_8H_{18}, B_9H_{15}, *i*-B_9H_{15}, $B_{10}H_{14}$, $B_{10}H_{16}$, α-$B_{10}H_{18}$, β-$B_{10}H_{18}$, $B_{10}H_{20}$, $B_{16}H_{20}$, $B_{18}H_{22}$, *i*-$B_{18}H_{22}$ and $B_{20}H_{16}$. In addition, a number of other hydrides have been reported, including two for which the formulae B_7H_{17} and $B_{20}H_{26}$ have been suggested, but the evidence for these is somewhat questionable. Of the known hydrides only B_5H_9, B_5H_{11}, B_6H_{10} and $B_{10}H_{14}$ were definitely characterized and reported in the original Mellor, although there was some evidence for B_6H_{12} and possibly for a hydride $B_{26}H_{36}$. (See also Note Added in Proof, p. 353).

The features of interest in the boranes are threefold. Firstly, they form a unique structural class of compounds, all of which can be described as being based on polyhedral clusters of boron atoms; the most important parent cluster is the icosahedron, and the boranes occur either as single fragments, or occasionally as a number of linked fragments. Secondly, these unusual structures pose problems of chemical bonding, which have necessitated the extension of molecular orbital theory in order to rationalize the observed geometrical structures and chemical stability of the compounds. Thirdly, the chemistry of the boranes is proving to be extensive and varied; it is probably best interpreted on the basis of considerable electron delocalization within the basic framework of any particular hydride. These features will be discussed at appropriate places throughout the Section.

The hydride anions form a related group of compounds as extensive and diverse as the parent neutral boranes themselves. The known anions fall into three classes:

(i) The $B_nH_n^{2-}$ series, of which the members $B_6H_6^{2-}$, $B_7H_7^{2-}$, $B_8H_8^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{11}^{2-}$ and $B_{12}H_{12}^{2-}$ have been characterized. The radical ion $\cdot B_8H_8^{-}$ has also been reported. The structure of these anions is usually based on complete (closed) polyhedra, and the bonding in them is similar to that in the hydrides themselves. Their chemistry implies extensive electron delocalization and can be compared in potential with aromatic carbon chemistry.

(ii) Those hydride anions derived structurally or chemically from known or hypothetical boranes. Members of this class include $B_5H_8^{-}$, $B_5H_{10}^{-}$, $B_6H_9^{-}$, $B_9H_{12}^{-}$, $B_9H_{14}^{-}$, $B_{10}H_{13}^{-}$, $B_{10}H_{12}^{2-}$, $B_{10}H_{14}^{2-}$, $B_{10}H_{15}^{-}$, $B_{11}H_{14}^{-}$ and $B_{11}H_{13}^{2-}$.

(iii) Those ions derived from linked boron hydride units, including $B_{18}H_{21}^{-}$, $B_{20}H_{18}^{2-}$ (two isomers), $B_{20}H_{19}^{3-}$ (two isomers), $B_{20}H_{18}^{4-}$ (three isomers) and $B_{24}H_{23}^{3-}$.

Closely related to the borane anions are the carboranes, in which one or more B^- units have been replaced by the isoelectronic carbon atoms, e.g. $B_nC_2H_{n+2}$. Carboranes which have no analogues in the anion series are also known, e.g. $B_4C_2H_8$, and an extensive derivative chemistry has been developed. These compounds and their corresponding anions and metal complexes are discussed separately in Section B8.

Boron frameworks containing heteroatoms other than carbon are also known. Although the icosahedral $B_{11}NH_{12}$ (isoelectronic with $B_{12}C_2H_{12}$ and $B_{12}H_{12}^{2-}$) has not yet been reported, derivatives with sulphur or phosphorus as the heteroatom are known, e.g. $B_9SH_{12}^-$, $B_{10}SH_{12}$, $B_{10}SH_{11}^-$, $B_{10}SH_{10}^{2-}$, derivatives of $B_{11}SH_{11}$, $B_{10}CPH_{11}$ and $B_{11}PH_{12}$. A recent development linking boron hydride chemistry with transition metal chemistry is the discovery that a number of boron cage compounds containing heteroatoms such as carbon or sulphur can act as π-ligands to transition metals, although as yet no π-complex has been found without a heteroatom in the boron framework. Compounds prepared include $Co(B_{10}H_{10}S)_2^-$, $Fe(B_{10}H_{10}S)_2^-$, $(B_{10}H_{10}S)CoC_5H_5$, $(B_{10}H_{10}S)Pt(PEt_3)_2$, $(B_{10}H_{10}S)Re(CO)_3^-$ and $(B_{10}H_{10}S)Co(PEt_3)_2$, together with numerous carborane derivatives mentioned in Section B8.

In the present Section the sequence of treatment proceeds systematically from lower to higher boranes and covers the structure, bonding, topology, electron distribution, physical properties, preparation and chemical properties, in that order. Passing reference will be made to related carboranes where this is appropriate.

Systematic nomenclature and numbering of the boranes and their derivatives are necessarily somewhat complicated. Detailed proposals have been made[1] and are best illustrated by examples as they arise. The main features are as follow:

1. The generic term for compounds of boron and hydrogen is 'borane'.

2. The number of boron atoms in the molecule is indicated by a Greek prefix and the number of hydrogen atoms by an Arabic numeral in parentheses directly following the name, e.g.

B_5H_9	pentaborane(9)
$B_{10}H_{16}$	decaborane(16)
$B_{18}H_{22}$	octadecaborane(22)
i-$B_{18}H_{22}$	*iso*-octadecaborane(22)

3. Polyboranes having closed structures (i.e. with boron skeletons which are complete polyhedra having all triangular faces) are designated by the italic prefix '*closo*-' which is a corruption of the Greek word for a cage, clovo; non-closed structures are designated '*nido*-' which is derived from the Greek word for a nest, e.g.

$B_{10}H_{14}$	*nido*-decaborane(14)
$B_{20}H_{16}$	*closo*-icosaborane(16)

4. Substituted boranes retain the original numerical suffix and substituents are listed alphabetically, e.g.

$B_{10}H_4I_{10}$	decaiododecaborane(14)
BBr_2F	dibromofluoroborane

5. For *nido*-boranes the boron atoms are numbered following plane projection drawings viewed from opposite the open portion of the framework; interior atoms are numbered first, then peripheral atoms, each set being numbered clockwise from '12 o'clock' on the drawing or the first position clockwise therefrom, as in Fig. 1.1.

6. For *closo*-boranes the boron atoms are numbered in sequential planes perpendicular to the longest highest-order axis; the atoms in each perpendicular plane are numbered clockwise from a reference plane through this symmetry axis. This rule also applies if addition of one skeletal atom produces a *closo*-structure having more than three planes of atoms perpendicular to the highest symmetry axis (see Fig. 1.2).

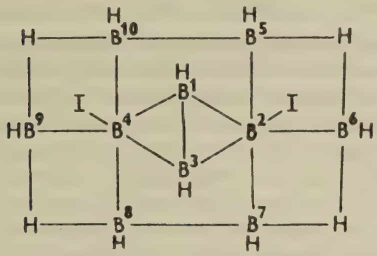


FIG. 1.1.—2,4-$I_2B_{10}H_{12}$; 2,4-diiododecaborane(14)

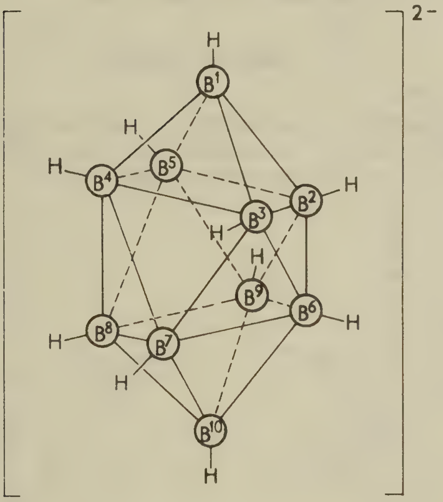


FIG. 1.2.—$B_{10}H_{10}^{2-}$; decahydro-*closo*-decaborate(2 –)

7. The use of symbols and numbers follows standard practices of organic nomenclature (see Fig. 1.1).

8. In BH_2 groups or substituted BH_2 groups the hydrogen atom or substituent which is directed away from the centre of the parent polyhedron is designated by the italic prefix '*exo-*' and the other by '*endo-*'.

9. Substituents in the bridge positions are designated by the symbol μ as a prefix to the name of the substituent.

10. Ions related to the boranes are named according to the rules for coordination compounds, the prefix 'hydro' being used independent of the polarity of the B–H bond; in cases of ambiguity the charge on the ion is indicated by a suffix in parentheses and the modifiers '*nido-*' and '*closo-*' can be added for clarity when required, e.g.

$LiBH_4$	lithium tetrahydroborate
$K_2[Zn_3(BH_4)_8]$	potassium octakis(tetrahydroborato)-trizincate(2 –)
$Na_2B_{10}H_{10}$	sodium decahydrodecaborate(2 –) or sodium decahydro-*closo*-decaborate(2 –)

For further details the full report[1] should be consulted.

Numerous reviews[2–18] and books[19–27] on the higher boranes and their derivatives have been published during the last decade, and these largely supersede earlier reviews.[28–31] The classic book by Stock[32] is still, however, of great historic interest.

Refs. p. 332

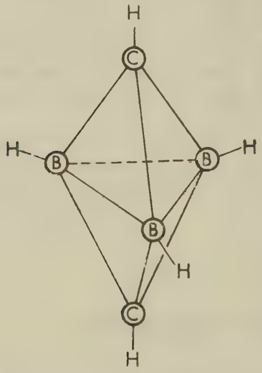
PART 2: STRUCTURAL FEATURES

With the advent of sophisticated techniques of structure determination, such as *X*-ray crystallography and electron diffraction, and particularly since the development of data-handling techniques by computers, a number of boron hydrides and their derivatives have had their structures determined unequivocally. Many others have been reasonably assigned by the less rigorous spectroscopic methods such as nuclear magnetic resonance (n.m.r.), microwave spectroscopy, and infra-red (i.r.) spectroscopy, and others have been indicated by chemical intuition, analogy and interpolation. A number of structural features emerge from the data, and the most important of these is the occurrence of large frameworks of boron and occasionally other atoms. These can be divided into (a) complete polyhedral frameworks, (b) polyhedral fragments and (c) linked polyhedra or polyhedral fragments. The ensuing discussion follows this sequence of presentation.

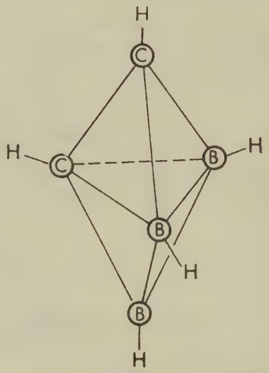
A. Complete Polyhedra

(1) FIVE-ATOM POLYHEDRA

The only five-atom polyhedra described so far have been two of the three possible isomeric carboranes $B_3C_2H_5$.[33–5] These have been shown to have the trigonal bipyramidal structures (1) and (2) by spectral evidence, and a number of alkylated derivatives of (1) have been postulated.[35–7] The isoelectronic $B_5H_5^{2-}$ ion has not yet been isolated.



(1)



(2)

(2) SIX-ATOM POLYHEDRA

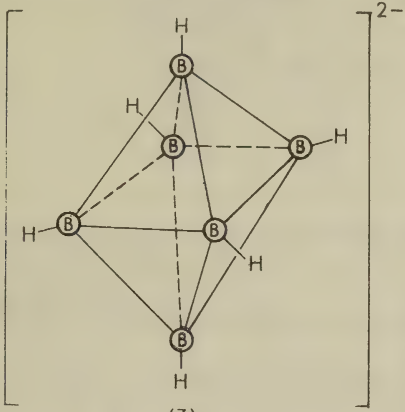
The ion $B_6H_6^{2-}$(3) has been investigated by *X*-ray analysis[38], and shown to be octahedral in the solid, with the average dimensions B–B 1·69 Å and B–H 1·11 Å. The available n.m.r. and i.r. data are also consistent with the octahedral structure in solution.[39] The two isomeric carboranes of formula $B_4C_2H_6$ are thought to be essentially octahedral, with carbon atoms *trans* (4) or *cis* (5) on the basis of n.m.r. evidence.[40] The structure of the carborane B_5CH_7 has not been definitely characterized, but an octahedral skeleton (6) with one bridging hydrogen has been tentatively suggested.[41]

(3) SEVEN-ATOM POLYHEDRA

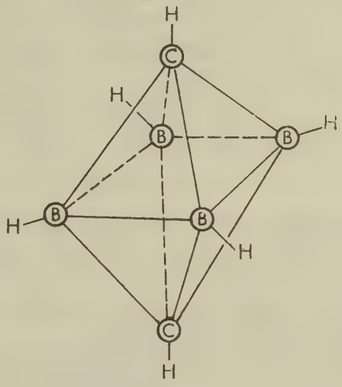
The $B_7H_7^{2-}$ ion (7) has been examined by n.m.r. in solution and the evidence of two boron environments in the ratio of 5:2 indicates the pentagonal bipyramidal structure, possibly through time-averaging.[42] The carborane $B_5C_2H_7$ was shown by microwave studies to have the bipyramidal structure (8) with dimensions as indicated.[43] The ^{11}B n.m.r. data were also consistent with this structure.[44] A number of alkylated derivatives of this system have been described.[37,45–6]

(4) EIGHT-ATOM POLYHEDRA

The ion $B_8H_8^{2-}$ was found by three-dimensional *X*-ray investigations to have a slightly distorted dodecahedral arrangement of boron atoms in the solid state[42,47]; this is shown in structure (9). The hydrogen atoms have been omitted from this and subsequent polyhedra for clarity. The boron atoms of one chemically and



(3)



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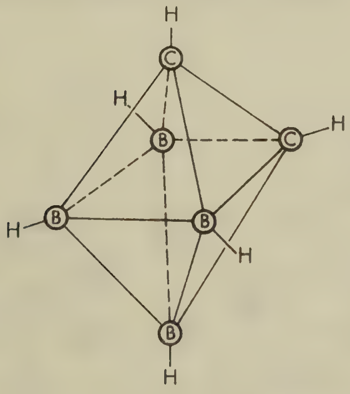

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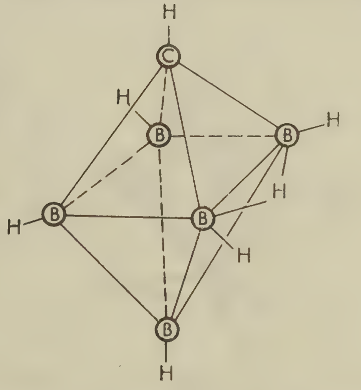

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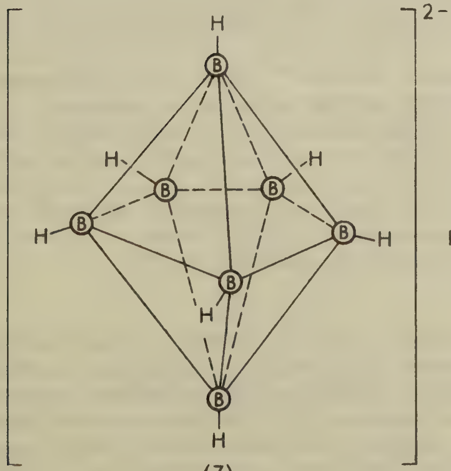

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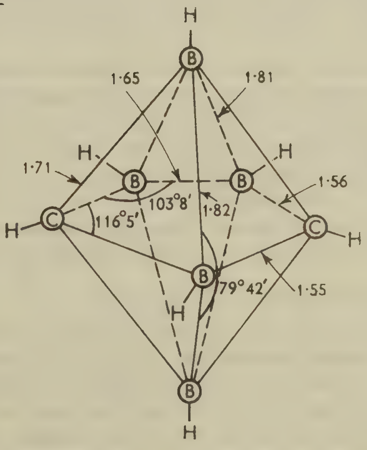


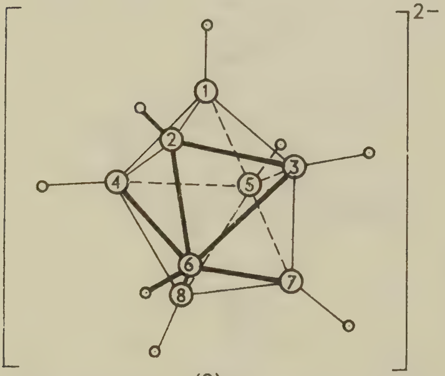
(8)

crystallographically equivalent set are six-coordinate ($B^3B^4B^5B^6$), while those of the other set are five-coordinate ($B^1B^2B^7B^8$). The distribution of B–B distances in $B_8H_8^{2-}$ and related polyhedra is given in Table 2.1 and can be correlated with the coordination numbers of the boron atoms involved, i.e. the shortest bond is between two five-coordinate boron atoms, the intermediate lengths are between five- and six-coordinate boron atoms, and the longest is between two six-coordinate borons. The distance of 1·56 Å between B^1 and B^2 is one of the shortest polyhedral B–B distances observed. Boron–hydrogen distances were less precisely determined but were in the expected range of 1·1–1·2 Å.

Table 2.1.—B–B Distances (Å) in B_8 Polyhedra

Bond type	$B_8H_8^{2-}$	$B_6H_6C_2Me_2$	B_8Cl_8
B^2–B^1	1·56	1·50	1·68
B^4–B^8	1·72	1·70	1·81
B^4–B^1	1·76	1·79	1·75
B^4–B^6	1·93	1·88	2·00

By contrast with the dodecahedral arrangement established by *X*-ray analysis, the ^{11}B n.m.r. spectrum of the $B_8H_8^{2-}$ ion in solution showed a single doublet suggesting equivalence of all the boron atoms. The n.m.r. data are consistent with the alternative square antiprism arrangement, although the two environments of the boron atoms in the dodecahedral arrangement do not differ grossly, and the n.m.r. equivalence may be fortuitous.[42] It is of interest that the neutral species B_8Cl_8 was originally described as a distorted square antiprism[48–9], but a recent refinement of the data indicates much closer agreement with the dodecahedral structure.[50]



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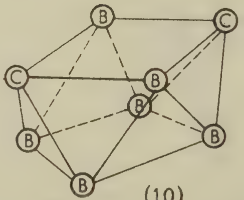

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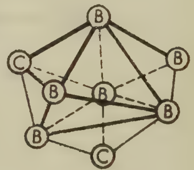


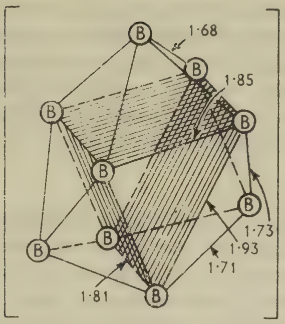
(11)

The electron-spin resonance (e.s.r.) spectrum of the ion radical $\cdot B_8H_8^-$ shows spectroscopic equivalence of all the boron and hydrogen sites[42], and possibly a similar situation occurs here.

The structure of $B_6C_2H_8$ has not been rigorously established, although n.m.r. evidence suggests the square antiprismatic geometry (10).[51] However, other workers have proposed the bisdisphenoid (dodecahedral) geometry (11).[52]

(5) NINE-ATOM POLYHEDRA

The ^{11}B n.m.r. and vibrational spectra of solutions of $B_9H_9^{2-}$ strongly indicate a tricapped trigonal prism of D_{3h} symmetry (12)[53] and this is confirmed in the solid by *X*-ray studies[54]; the average B–B bond distance is 1·78 Å and various interatomic distances (±0·015 Å) are indicated in structure (12). B–H distances vary between 1·07 and 1·27 Å (±0·15 Å). The data on B_9Cl_8H are more consistent with a square-capped antiprism of C_{4v} symmetry (13).[55] The ^{11}B n.m.r. of a derivative of $B_7C_2H_9$



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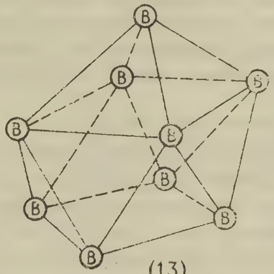
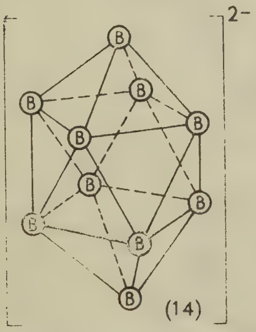


(13)

is consistent with the tricapped trigonal prismatic geometry in which the carbon atoms occupy apices.[51]

(6) TEN-ATOM POLYHEDRA

^{11}B n.m.r. studies on solutions of $B_{10}H_{10}^{2-}$ [56–7], and the general features of the infra-red and Raman spectra of the ion[58] are wholly consistent with the *X*-ray data of the crystalline copper(I) salt[59] in which the geometry is that of a bicapped square antiprism of D_{4d} symmetry (14). The interatomic distances are: B^1–B^2 1·73 Å, B^2–B^3 1·86 Å and B^2–B^6 1·81$_5$ Å. Furthermore, the ^{11}B n.m.r. data of two isomers



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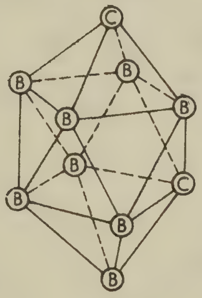

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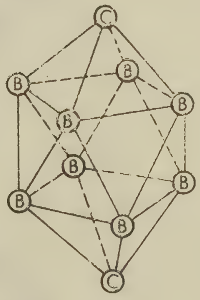
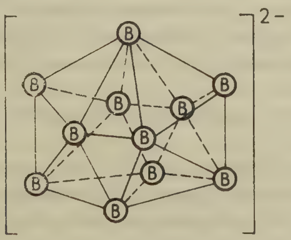


(16)

of derivatives of $B_8C_2H_{10}$ suggest the bicapped square antiprism structure with the carbon atoms at the 1,6- and 1,10-positions, respectively (15 and 16).[51] Similarly, n.m.r. data for $B_9CH_{10}^-$ suggest the bicapped square antiprism with the carbon atom at the apex position.[60]

(7) ELEVEN-ATOM POLYHEDRA

Although the structure of the $B_{11}H_{11}^{2-}$ ion has not been rigorously established, the ^{11}B n.m.r. spectrum consists of two doublets of relative intensity 10:1, and the data are consistent with an ion of C_{2v} symmetry (17).[53] This geometry has been established in the case of derivatives of $B_9C_2H_{11}$ (18) both by spectral data[61–2] and



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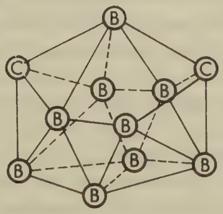
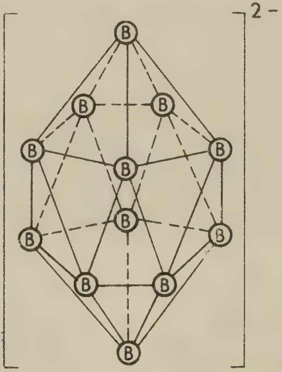


(18)

by *X*-ray analysis.[63] It is presumed that the isoelectronic $B_{10}CH_{11}^-$ ion is also isostructural with these.[60] Similar framework structures have also been proposed for $B_{10}H_{12}AlH_2^-$[64], $B_{10}GaH_{16}^-$[64], and $(Et_2O)_2CdB_{10}H_{12}$[65], though a more recent single-crystal *X*-ray structure determination has shown this last compound to be dimeric; two diagonally opposite bridge hydrogen atoms in each B_{10} unit are replaced by the two cadmium atoms, which thereby bridge the two decaborane clusters[65a] (see p. 299).

(8) TWELVE-ATOM POLYHEDRA

X-Ray analysis of single crystals of $K_2B_{12}H_{12}$ has established the full icosahedral structure (19) for the $B_{12}H_{12}^{2-}$ ion, although a small distortion in the solid state was noted[66]; the structural parameters obtained were 6 B–B distances of 1·755 Å, and 24 B–B distances of 1·780 Å. The vibrational spectra in solution are also in complete accordance with the icosahedral structure.[58] Likewise, there have been a number of *X*-ray and electron diffraction studies on carboranes of the type $B_{10}C_2H_{12}$ and derivatives[67–79], and the near icosahedral geometry has been established. The three possible geometric isomers are all known and are represented by structures (20), (21), and (22). They have been called the *ortho*(1,2), *meta*(1,7)[80] and *para*(1,12)[81] derivatives, respectively.



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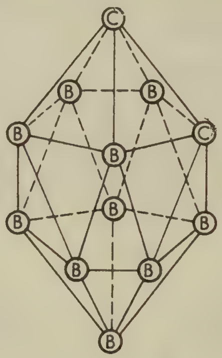

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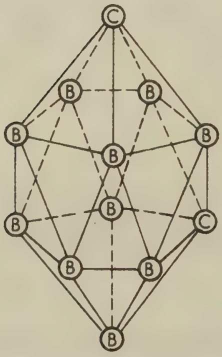

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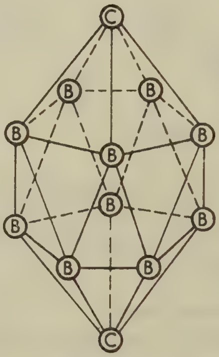

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Some average structural parameters for a number of C_{2v} 1,2-carboranes are given in Table 2.2.

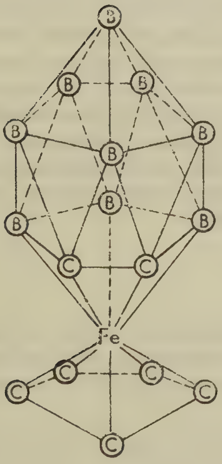
Although the ion $B_{11}CH_{12}^-$ has not been examined by *X*-ray crystallography, the n.m.r. data are consistent with an icosahedral structure.[60] The icosahedral structure has also been proposed for a number of species containing other hetero-atoms. The stereochemistry of $C_6H_5B_{11}H_{10}S$ and $(C_6H_5)_2B_{11}H_9S$ has not yet been rigorously established, but is probably icosahedral.[82] Similarly, two isomers (1,2- and 1,7-) of

Table 2.2.—Interatomic Bond Distances in some C_{2v} Carboranes[74]

Bond position	No. of equivalent bonds	1,2-$B_{10}H_{10}C_2(CH_2Br)_2$	1,2-$B_{10}Cl_8H_2C_2H_2$	1,2-$B_{10}Br_2H_8C_2H_2$
1–2	1	1·64	1·67	1·63
1–3	4	1·71	1·73	1·71
1–4	4	1·73	1·70	1·73
4–5	2	1·79	1·79	1·80
3–8	2	1·76	1·75	1·73
3–4	4	1·78	1·81	1·76
4–8	4	1·75	1·78	1·74
8–9	4	1·77	1·81	1·78
9–12	1	1·81	1·82	1·73
4–9	4	1·75	1·76	1·76

$B_{10}CPH_{11}$ have been reported, and the presumably icosahedral $B_{11}H_{11}PC_6H_5$ has been isolated.[83]

A number of metallocarboranes and metallothiaboranes have been prepared, and the essentially icosahedral nature of a number of these (23–5) have been confirmed[84–6], although the carbon atoms in (24) were found to be disordered among the pentagons adjacent to the cobalt.[86]



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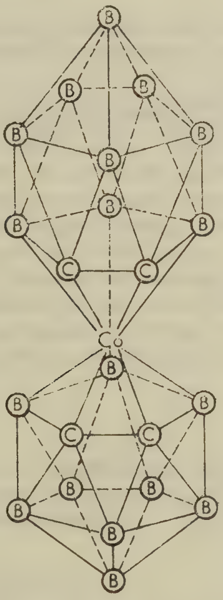

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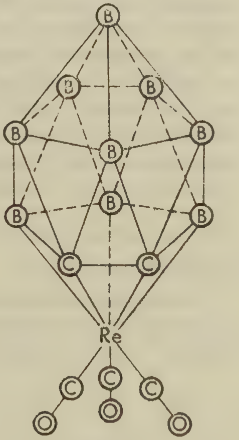

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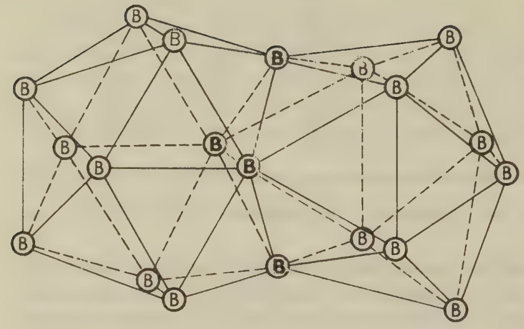
(9) TWENTY-ATOM POLYHEDRA

The hydride $B_{20}H_{16}$ was independently discovered by two groups of investigators and its structure has been shown to contain the boron framework shown in (26).[87–90] The structure consists of two decaborane-like cages fused perpendicularly across their open faces. Terminal hydrogens are bonded to all but the four connecting borons (shown in bold face type), and there are no bridge hydrogens.

The species $B_{20}H_{16}(NCCH_3)_2,CH_3CN$, which is obtained from $B_{20}H_{16}$, was found[91–2] to have a different geometry from that of the parent hydride, and can be considered as B_{11} and B_{12} species fused by a common triangle of boron atoms. The structure is shown in (27): the three connecting boron atoms are shown in bold face and the two L represent coordinated acetonitrile. The third CH_3CN molecule is



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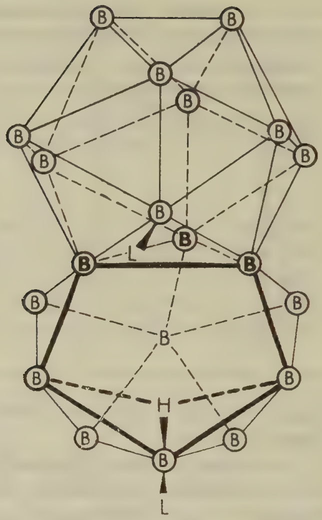


(27)

present in the crystal as solvate. Only the unique hydrogen atom is shown, the other fifteen being terminal hydrogen atoms on the fifteen non-bridging and non-coordinated boron atoms.

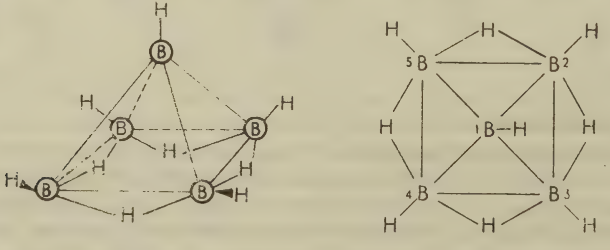
B. Polyhedral Fragments

The structures of a large number of the boranes and *nido*-carboranes comprise fragments of the polyhedra already described. An important feature of these structures is the existence of bridging-hydrogen atoms, and these normally occur at edges of the polyhedral fragments in the general region of space which would have been occupied by the missing boron atoms in the completed polyhedra. The most important polyhedron from which fragments are derived is the icosahedron, although for pentaborane(9) the octahedron is the parent polyhedron. For the sake of clarity, two-dimensional diagrams are useful for indicating hydrogen arrangements, and these are shown in addition to the three-dimensional structure.

(1) FIVE-ATOM CLUSTERS

Pentaborane(9), B_5H_9

The accepted structure (28) for pentaborane(9) was determined by *X*-ray crystallography[93–4], and independently by electron diffraction in conjunction with i.r. and entropy data[95–7], and was further confirmed by microwave studies.[98–9] However,



(a)

(b)

		Å
B–H	terminal	1·22
B–H	bridge	1·35
B^1–B^2		1·69
B^2–B^3		1·80

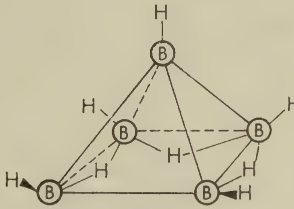
(28)

earlier studies had led to erroneous conclusions.[100,101] Vibrational studies and normal-coordinate analysis of B_5H_9 have been carried out.[97,102]

The tetragonal pyramidal structure has been further confirmed in 1-iodopentaborane(9)[103–4] and 2,3-dimethylpentaborane(9)[105] by *X*-ray methods.

The Octahydropentaborate(1−) Ion, $B_5H_8^-$

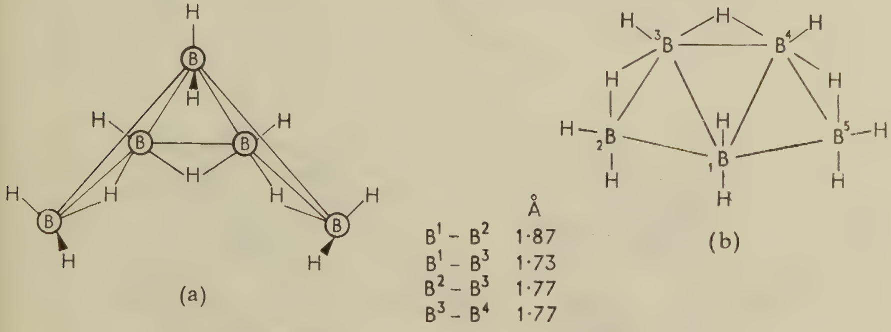
The structure of the $B_5H_8^-$ ion has not been unequivocally determined, but n.m.r. evidence[106] suggests little change from the pentaborane(9) structure. The results are best interpreted as loss of a bridge hydrogen from B_5H_9, the equivalence of the basal boron atoms being interpreted on the basis of rapid tautomerism of the bridge hydrogens in structure (29).



(29)

Pentaborane(11), B_5H_{11}

The structure of pentaborane(11) (30) was shown to be an icosahedral fragment by *X*-ray crystallography[107–9], although there was slight uncertainty in the positions of the hydrogen atoms. The boron positions were confirmed by electron diffraction.[110] Previous electron diffraction study gave incorrect results.[111]



(a)

	Å
B^1-B^2	1·87
B^1-B^3	1·73
B^2-B^3	1·77
B^3-B^4	1·77

(b)

(30)

(2) SIX-ATOM CLUSTERS

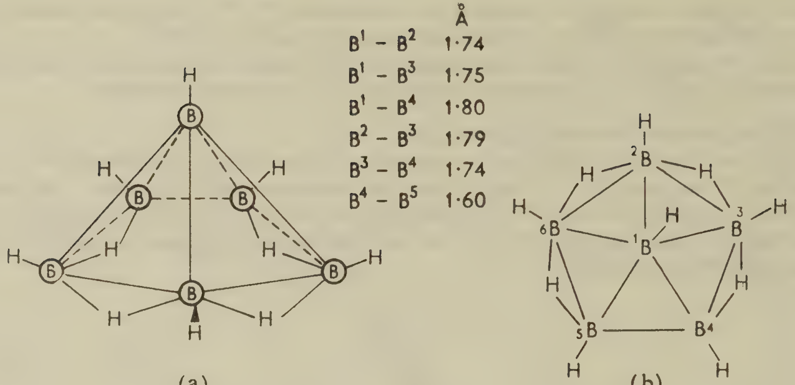
Hexaborane(10), B_6H_{10} *and its derivatives*

The structure of hexaborane(10) was shown by *X*-ray crystallography[112–15] to be a pentagonal–pyramidal fragment of an icosahedron, and the data have been refined[116] to show structure (31) conclusively in the crystalline state.

Very recently[117] hexaborane has been deprotonated to give the new anion $B_6H_9^-$, which is formed by loss of a bridge proton from B_6H_{10}. The ^{11}B n.m.r. spectrum shows two doublets with an intensity ratio of 1:5 implying that all five basal boron atoms become magnetically equivalent by bridge–proton exchange.

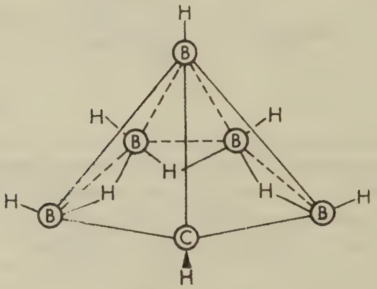
Another recent development is the isolation of the *nido*-carborane, B_5CH_9, which is the first member of a new series B_nCH_{n+4} to be prepared.[118] Its n.m.r. spectrum strongly implies structure (32). Various methyl and other alkyl derivatives are also known.[119,120]

Closely related to the structure of hexaborane(10) is that of 2,3-dicarba-*nido*-hexaborane(8) $B_4C_2H_8$ (33) and its C,C′-dimethyl derivative, for which *X*-ray deter-



	Å
B^1-B^2	1·74
B^1-B^3	1·75
B^1-B^4	1·80
B^2-B^3	1·79
B^3-B^4	1·74
B^4-B^5	1·60

(31)



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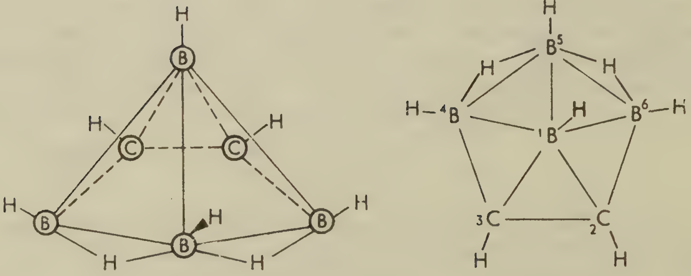


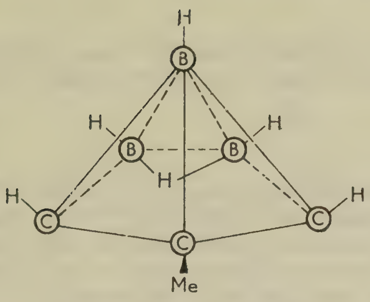
(a) (33) (b)

minations have been carried out.[121–2] The interesting molecular parameters are the short C–C distances of 1·419 and 1·431 Å in the parent carborane and the dimethyl derivative, respectively, and the B–C distances of 1·507 and 1·514 Å. The B–B distances ranged from 1·70–1·80 Å in both compounds.[122]

The isoelectronic sequence of structures B_6H_{10}, B_5CH_9 and $B_4C_2H_8$ has been extended to alkyl derivatives of $B_3C_3H_7$[123] and $B_2C_4H_6$[124] though the parent carboranes have not yet been prepared. On the basis of n.m.r. and i.r. spectra it appears that these compounds have the *nido*-hexaborane(12) skeleton, but with three and four fewer bridging-hydrogen atoms, respectively, as shown in structures (34) and (35).

Hexaborane(12), B_6H_{12}

Several structures have been suggested for hexaborane(12)[125], and although no definitive crystallographic study has yet been made, n.m.r. studies indicate the probable structure (36).[126–8]



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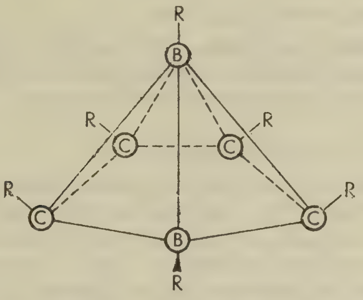

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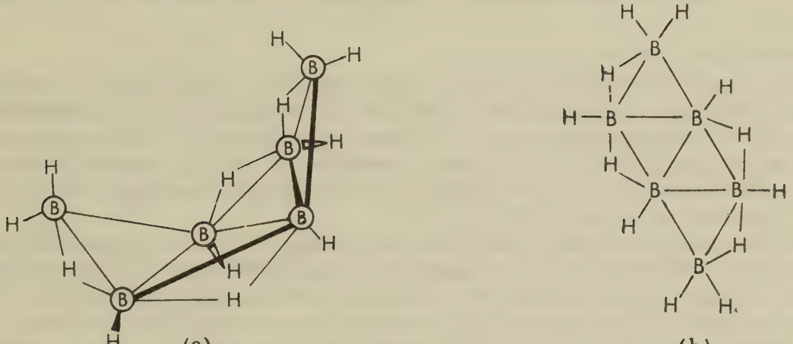

(a)

(36)

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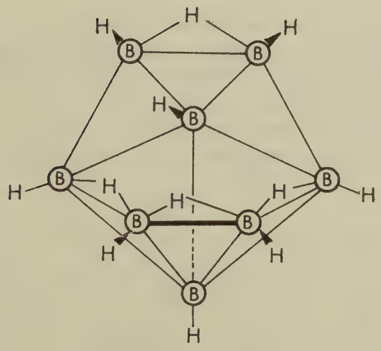

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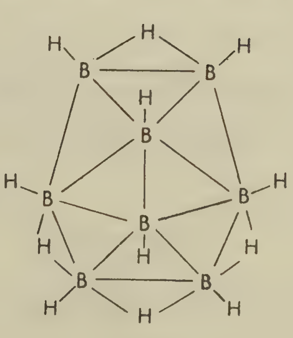

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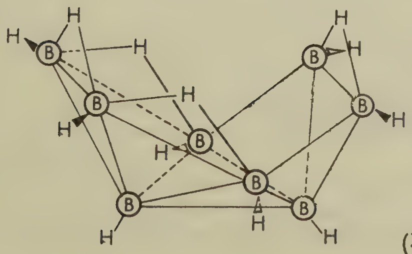


(37)

(3) SEVEN-ATOM CLUSTERS

There have been a few tentative reports of heptaboranes from mass spectral evidence but it is unlikely that any *nido*-heptaborane has yet been prepared, and certainly no structural evidence exists.

(4) EIGHT-ATOM CLUSTERS

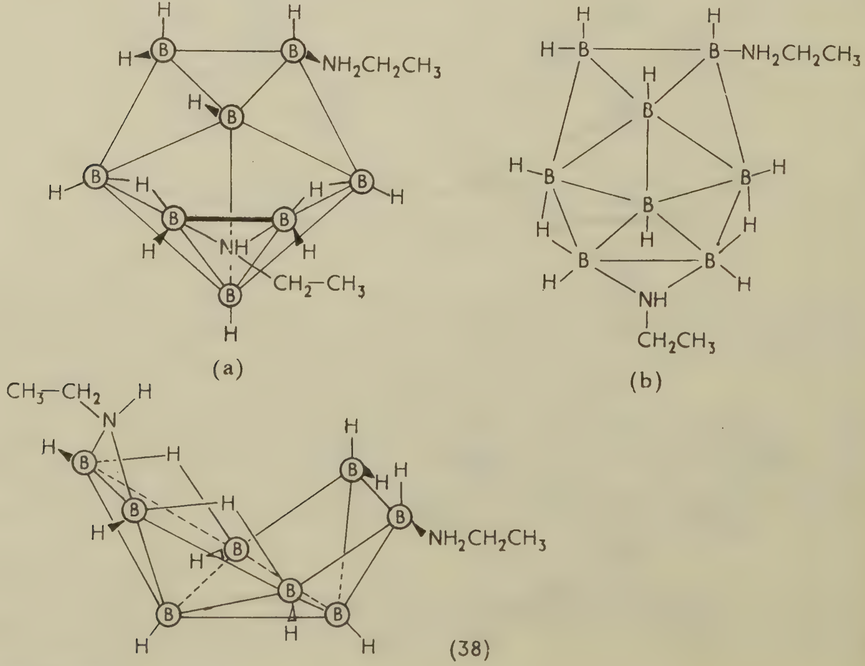
Three octaboranes have been reported in the literature, B_8H_{12}[129, 130–1], B_8H_{14}[132–3], and B_8H_{18}[134–5], and one derivative of the hypothetical $B_8H_{13}^-$ ion.[136–8] The structure of B_8H_{18} is discussed under linked polyhedra and the structure of B_8H_{14} has not yet been established. The *X*-ray crystallographic investigation of B_8H_{12} has shown it to be an icosahedral fragment (37, shown in two presentations for clarity)[129, 130] which can be visualized as being derived from decaborane(14) by removal of boron atoms 9 and 10. In the structure of $EtNH_2B_8H_{11}NHEt$ (38, also shown in two ways), the boron atoms have essentially the same partial icosahedral arrangement as in B_8H_{12} with the hydrogen arrangement anticipated for the hypothetical $B_8H_{13}^-$ ion.

(5) NINE-ATOM CLUSTERS

Two isomers of nonaborane(15) have been reported, although there is crystallographic evidence for the structure of only one of these, B_9H_{15}.[139–42] The structure is that of an icosahedral fragment (39) formed by removal of boron atom number 10 from decaborane(14). The ^{11}B n.m.r. spectrum of *i*-B_9H_{15} suggests a structure with approximate C_{3v} symmetry derived by removal of a triangle of boron atoms from a complete icosahedron.[143]

The dicarbanonaborane(13), $B_7C_2H_{13}$, and a number of its derivatives have been prepared[144], and the n.m.r. data suggest an icosahedral fragment with methylene groups as shown in structure (40). This has recently been confirmed by *X*-ray crystallography.[145] The relation of the proposed structure of *i*-B_9H_{15} is clear.

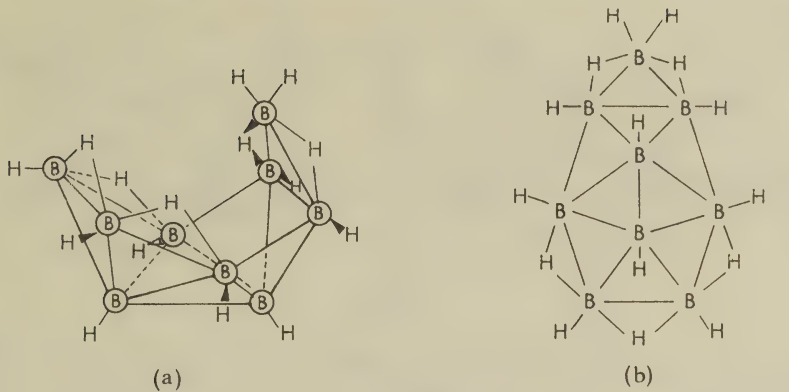
A similar icosahedral fragment has recently been established by *X*-ray crystallography for the ion $B_9H_{14}^-$.[146] It can be thought of as being formed by the removal of B^9 (rather than B^{10}) from decaborane(14), i.e. by removal of a triangular face from



(a)

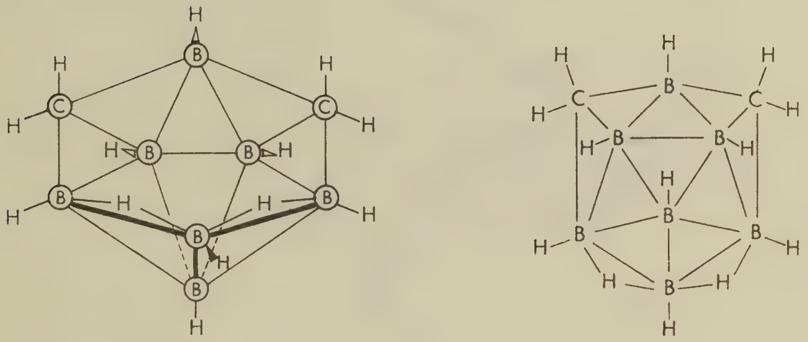
(b)

(38)



(a) (b)

(39)



(a) (40) (b)

the completed icosahedron rather than removal of a linear chain of three boron atoms as was found for B_9H_{15}. The structure is shown in (41).

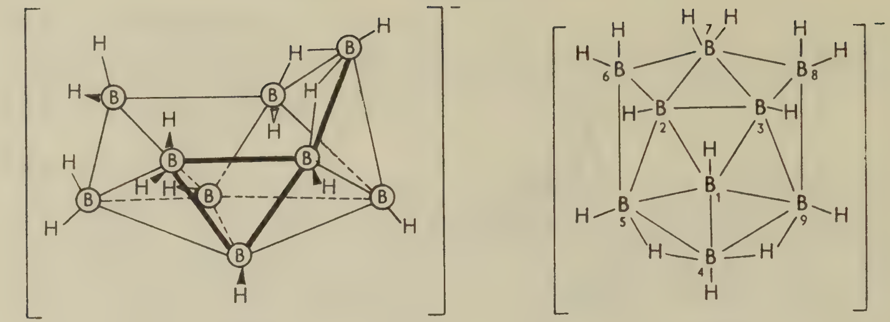
The isoelectronic adduct $MeCNB_9H_{13}$ has the same skeletal arrangement of boron atoms but a differing arrangement of BH_2 and BHB groups as shown in structure (42).[147–8] The structure of the $B_9H_{12}^-$ ion has not been established, although two feasible structures have been suggested.[149]

(6) TEN-ATOM CLUSTERS

Decaborane(14), $B_{10}H_{14}$ *and its Derivatives*

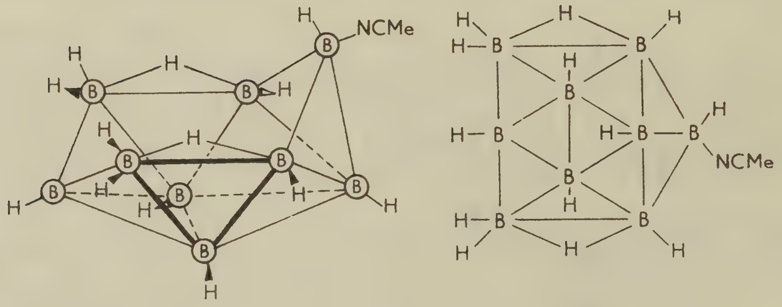
Decaborane has been the subject of a number of structural investigations. The original electron diffraction study[150] gave the correct boron arrangement but the hydrogen arrangement was incorrectly assigned. However, reinvestigation of these data showed them to be consistent with the correct structure[151], and other workers have found similar results.[152] After some early discussions[153] single-crystal *X*-ray studies gave the structure unambiguously[154–5] as an icosahedron with two adjacent boron positions missing (43). The structural parameters were found to be: B^1–B^3, 1·71; B^1–B^2, 1·78; B^2–B^5, 1·76; B^2–B^7, 1·80; B^5–B^6, 1·77; B^2–B^6, 1·72; B^1–B^5, 1·78; B^3–B^7, 1·77; and B^5–B^{10}, 2·01 Å. A recent neutron diffraction study has given the hydrogen atom positions with greater accuracy.[155a] Icosahedral fragment geometry has also been found in 1-iododecaborane[156], 2,4-di-iododecaborane[157] and 1-ethyldecaborane.[158]

Only preliminary single-crystal work has been carried out on the compounds $NaB_{10}H_{13}.Et_2O$ and $NaB_{10}H_{13}.2Me_2O$[159] and the structure of the $B_{10}H_{13}^-$ ion remains in doubt, although a topological representation has been proposed.[20, 31] There



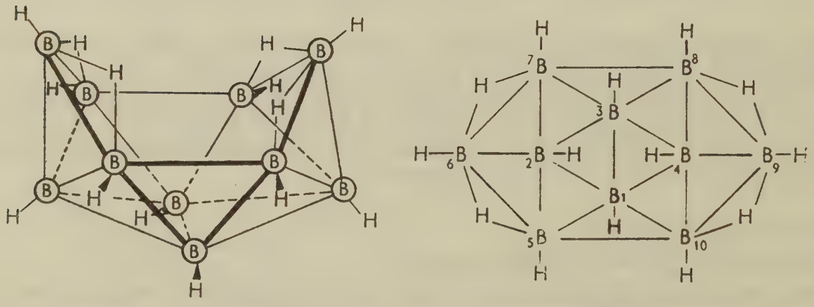
(a) (b)

(41)



(a) (b)

(42)



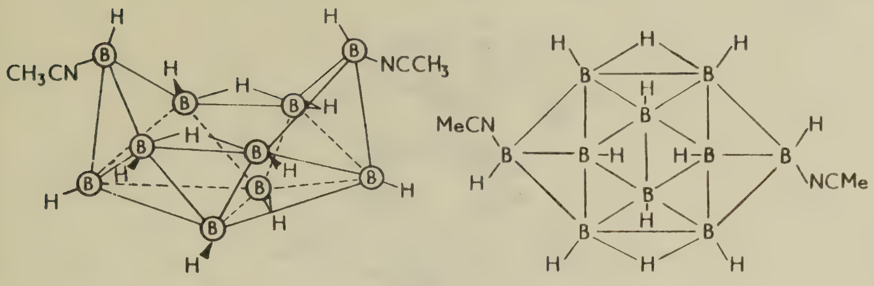
(a) (b)

(43)

is no information on the structure of $B_{10}H_{12}^{2-}$. ^{11}B n.m.r. data are rather uninformative on the structure of the $B_{10}H_{15}^{-}$ ion[160], and although two possible structures have been suggested[149], no conclusion has yet been reached. The structures of the derivatives of $B_5C_5H_9$ have not yet been rigorously established.[161]

The Tetradecahydrodecaborate(2−) Ion, $B_{10}H_{14}^{2-}$ *and its Derivatives*

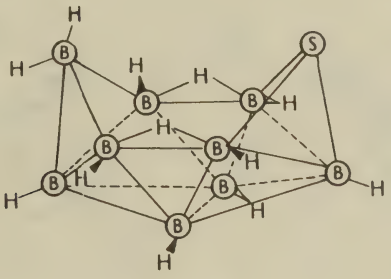
The structure of the $B_{10}H_{14}^{2-}$ ion has been inferred from an examination of its ^{11}B n.m.r. spectrum[162], and although an *X*-ray crystallographic study on the ion itself has not been carried out, its formal derivatives $(MeCN)_2B_{10}H_{12}$ and $(2\text{-}BrC_5H_4N)_2B_{10}H_{12}$ have been examined.[163–6] The boron framework is similar to that in neutral decaborane(14), but the bridge hydrogen arrangement is different (44).



(a) (b)

(44)

The structure of the thiaborane anion in $Cs^+B_9H_{12}S^-$ has been proposed on the basis of n.m.r. evidence to be related to that of $B_{10}H_{14}^{2-}$ by replacement of the BH_2^- group at position 6 with the 'isoelectronic' S atom.[167] This structure (45) has recently been confirmed by *X*-ray crystallographic investigation of the complex $(Ph_3P)_3Au^+B_9H_{12}S^-$.[168]



(45)

(7) ELEVEN-ATOM CLUSTERS

No neutral B_{11} boron hydride has yet been described, although the ions $B_{11}H_{14}^-$ and $B_{11}H_{13}^{2-}$ have been isolated. On the basis of the exceedingly simple ^{11}B n.m.r. spectra of $B_{11}H_{14}^-$, the structure (46) was proposed, in which the open position of the $B_{11}H_{11}^{2-}$ unit (an icosahedron with one boron atom missing) was bonded to a triangular H_3^+ unit.[169, 170] A recent crystallographic study[171] of $Cs^+Me_4N^+B_{11}H_{13}^{2-}$ showed the $B_{11}H_{13}^{2-}$ ion to have structure (47), in which the hydrogen-bridged B–B distance is 1·89 Å, the other B–B distances in the open face are 1·80 and 1·83 Å, and the remaining B–B distances range from 1·72–1·83 Å. $B_9C_2H_{13}$ has been described[172], and although this is almost certainly an icosahedral fragment, no detailed structure has been reported. Likewise for the two isomers of $B_9C_2H_{12}^-$[173] in which the carbon atoms occupy *ortho* and *meta* positions in the open face. A similar structure (48) has been proposed for the anion in $Cs^+B_{10}H_{11}S^-$ on the basis of n.m.r. data. By contrast, $B_9C_2H_{11}$ has the *closo*-structure already described on p. 241.

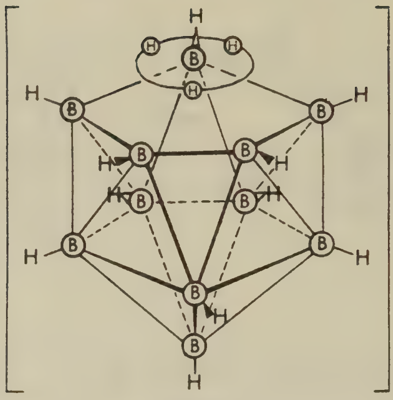
C. Linked Polyhedra and Polyhedral Fragments

(1) EIGHT-ATOM SPECIES

The structure of octaborane(18) was suggested on the basis of n.m.r. evidence to be two tetraborane units linked through a B–B bond[134–5], and this structure, (49), has recently been confirmed by mass spectrometry.[174]

(2) TEN-ATOM SPECIES

The structure of $B_{10}H_{16}$ was shown[175] by *X*-ray crystallography to be two pentaborane(9) units linked by a B–B bond through the apices (50). The structure has



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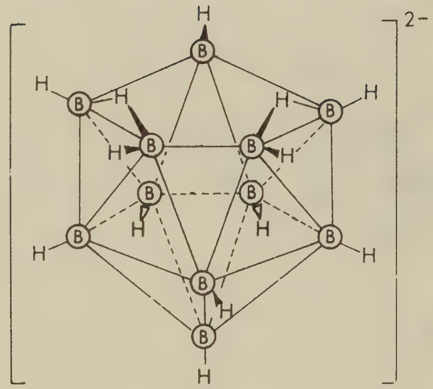
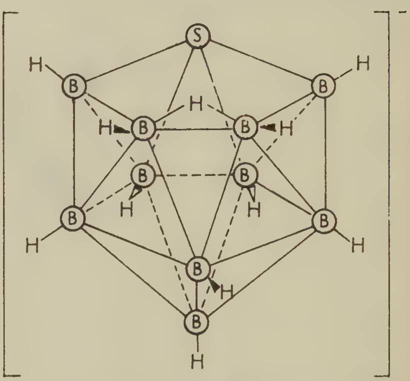


(47)



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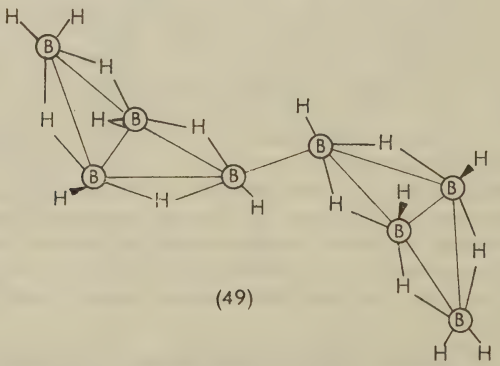
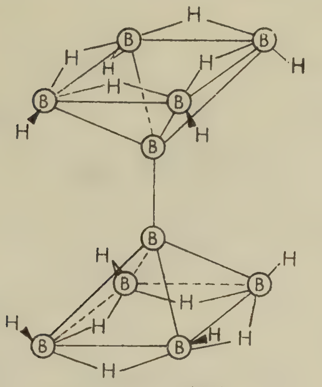


(49)

D_{4h} symmetry and the B–B distances are 1·74 Å for the linking bond, 1·76 Å for the slant-edge, and 1·71 Å for the basal borons.

(3) SIXTEEN-ATOM SPECIES

The new borane $B_{16}H_{20}$ is the first to have no elements of molecular symmetry.[176] *X*-Ray diffraction establishes structure (51) which can be thought of as a B_{10} icosahedral fragment which shares an edge (originally occupied by a bridging proton in decaborane) with a B_8 fragment in such a way that the two fragments open in opposite directions. The B–B bond distances are in the range 1·7–1·8 Å except for the



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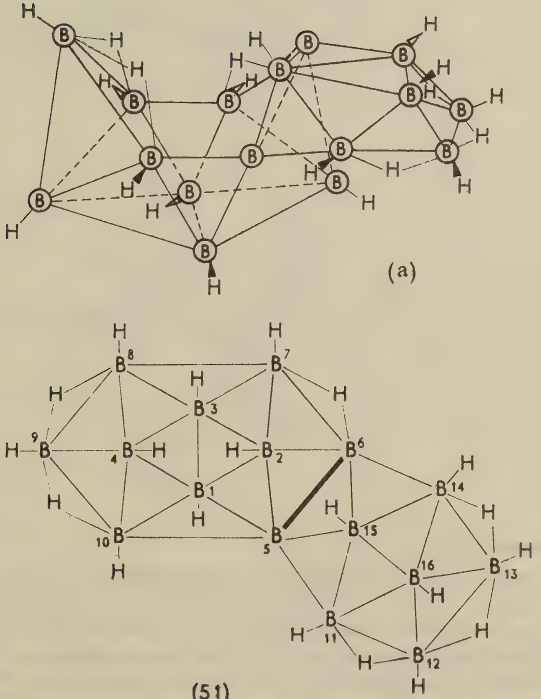
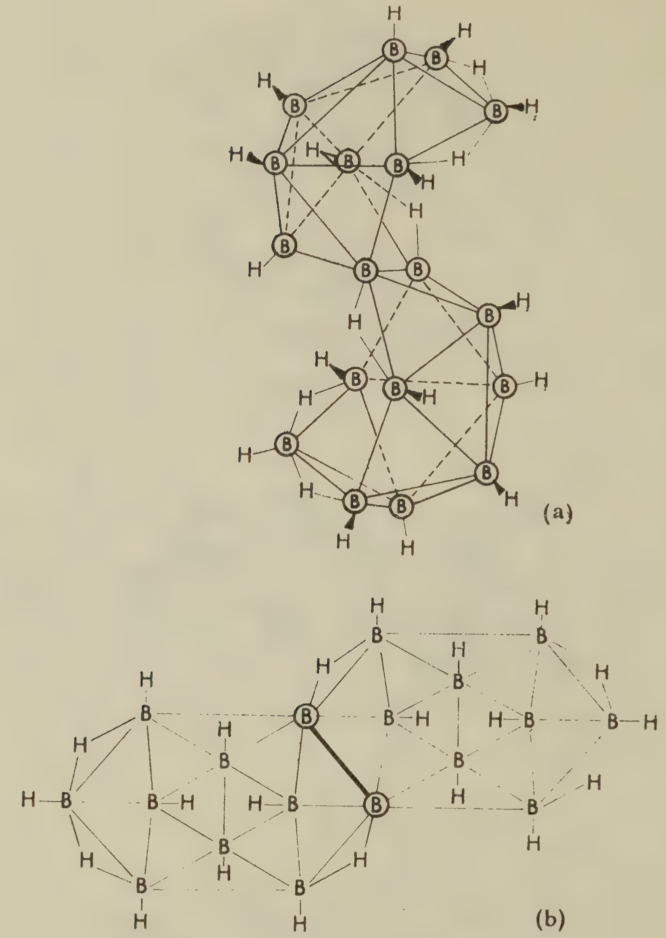


(51)

expected short B^5–B^6 value of 1·68 Å and the predictably large values of 1·91 and 2·02 Å for B^5–B^{10} and B^7–B^8 respectively. The average values for the B–H distances of 1·1 and 1·3 Å for the terminal and bridging hydrogen atoms are also consistent with values for other boranes.

(4) EIGHTEEN-ATOM SPECIES

The structures of $B_{18}H_{22}$ and *i*-$B_{18}H_{22}$ have been determined crystallographically, and have been shown to be essentially two decaborane-like cages fused along an edge.[177–81] These are exemplified in structures (52) and (53). The structure of the $B_{18}H_{21}^-$ ion has not been established, but is probably related to that of $B_{18}H_{22}$ by loss of a bridge hydrogen.

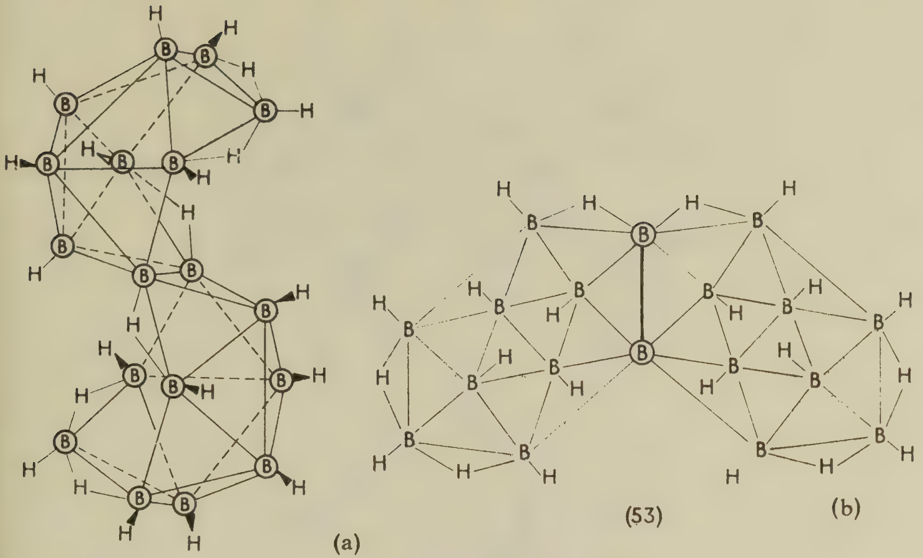


(52)

(5) TWENTY-ATOM SPECIES

The probable structure of the $B_{20}H_{18}^{2-}$ ion was derived from an examination of the 60 MHz ^{11}B n.m.r. spectra[182], and this was recently confirmed by *X*-ray analysis.[183] The structure comprises two coupled B_{10} polyhedra (54) with B–B distances comparable to those found in $Cu_2B_{10}H_{10}$. Photo-isomerization of the $B_{20}H_{18}^{2-}$ ion yielded another isomeric species $B_{20}H_{18}^{2-}$, to which on the basis of ^{11}B n.m.r. and preliminary single-crystal *X*-ray diffraction was assigned the structure (55).[184] This has recently been confirmed by a complete *X*-ray structure determination.[185] The average apical–equatorial distance is 1·68 Å and the average equatorial–equatorial distance 1·82 Å; the shortened interbridging boron–boron distances average $1{\cdot}68_5$ Å and the B–B distances across the B–H–B bridges average 2·04 Å.

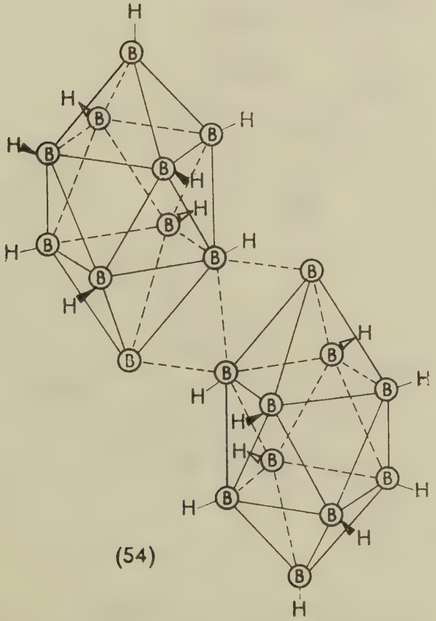
A preliminary study of $B_{20}H_{16}.[(CH_3)_2S]_2$ by *X*-ray diffraction located the positions of the boron atoms[186], and it was proposed that the ligands occupied apical positions. The ion $B_{20}H_{19}^{3-}$ was suggested to be two B_{10} polyhedra linked by a bridging hydrogen. Of the three possible isomers (axial–axial, axial–equatorial, or equatorial–equatorial linking), two isomers could be isolated of which only the most stable could be investigated by n.m.r. methods, and this was suggested to be the axial–equatorial linked isomer[186–7], structure (56). The three isomers of the $B_{20}H_{18}^{4-}$ ion were shown to be two B_{10} polyhedra bonded through a single boron–boron



(a)

(53)

(b)

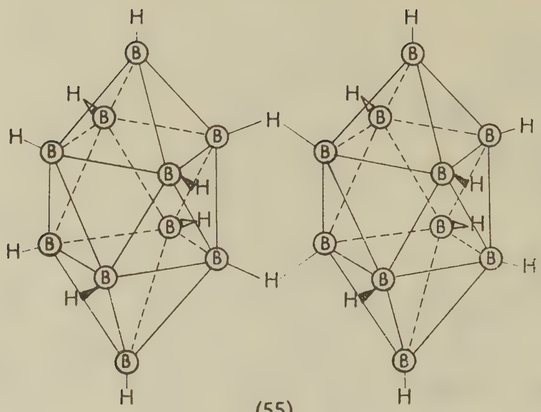


(54)

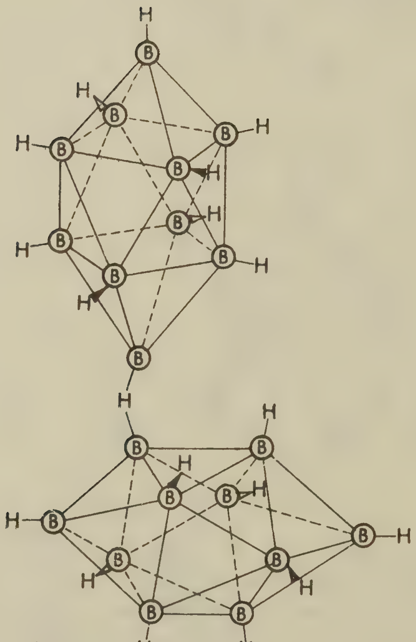
linkage in the three possible ways axial–axial (57), axial–equatorial (58), or equatorial–equatorial (59).[187] The hydride $B_{20}H_{26}$ has been reported from the deuteron irradiation of $B_{10}H_{14}$[188-9], and it is possible that this indicates two linked decaborane units.

(6) TWENTY-ONE ATOM SPECIES

The ions $[M(B_{10}H_{12})]^{2-}$ (M = Zn, Cd and Hg) are isostructural, and a detailed single-crystal *X*-ray analysis of $[Ph_3PMe^+]_2[Zn(B_{10}H_{12})_2]^{2-}$ has shown that the



(55)



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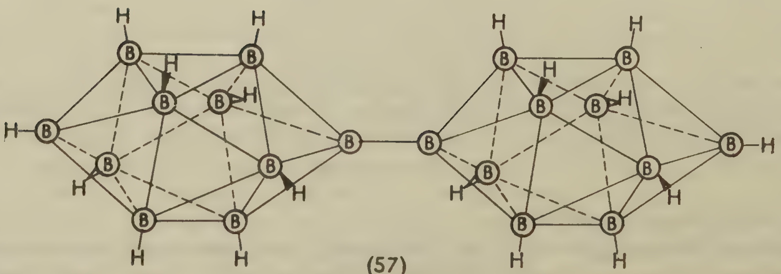

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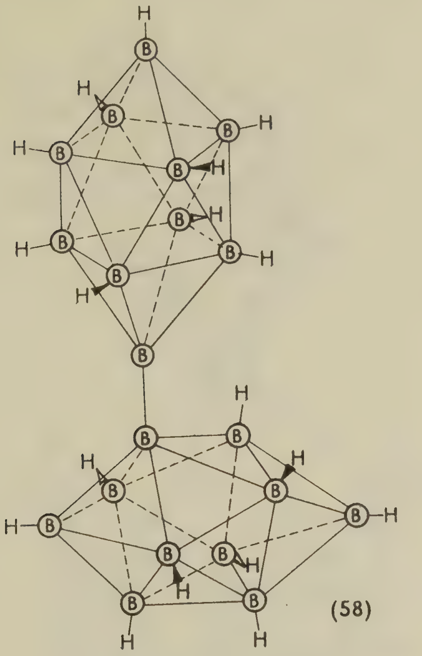

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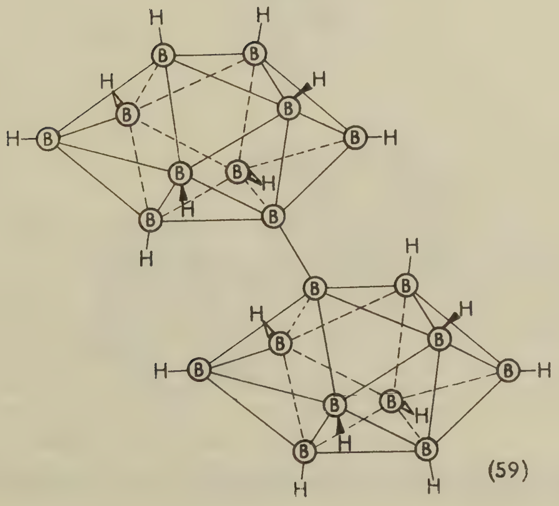


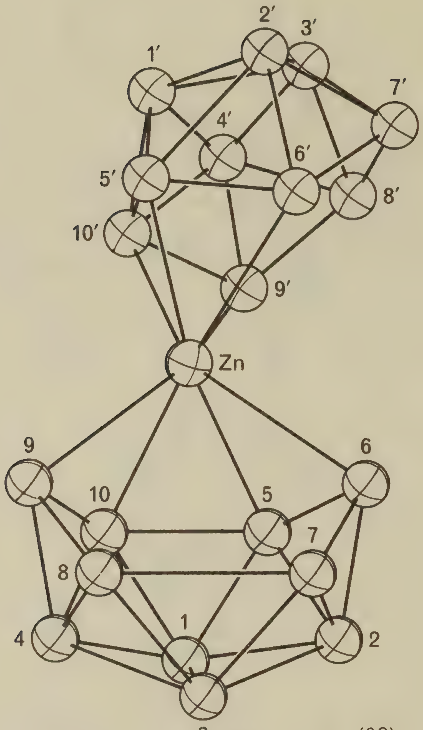
(59)

structure of the anion is as given in (60)[189a]. The structure of the corresponding nickel complex, (61), is similar except for the expected difference of orientation of the two chelating borane clusters[189b].

(7) TWENTY-FOUR ATOM SPECIES

Electrochemical oxidation of $B_{12}H_{12}^{2-}$ was reported to yield[190] $B_{24}H_{23}^{3-}$; the structure is considered to be 1,1′-μ-hydro-bis(undecahydro-*closo*-dodecaborate)(3−) as shown in (62).[191]

General papers on the structures of boranes have been published.[191a,b,c,d] Details of construction of models of boron hydrides have been described.[192,192a] A variety



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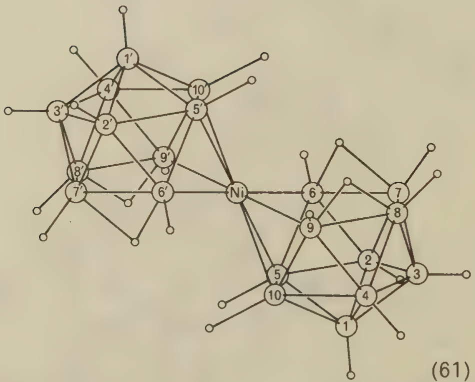
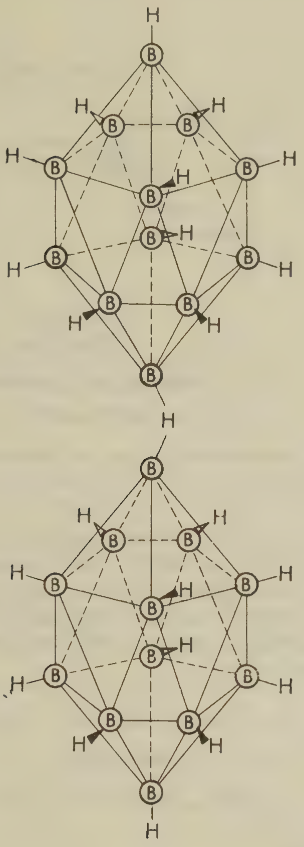


(61)

of boron hydride derivatives have been examined by *X*-ray diffraction to yield powder patterns.[193]

PART 3: BONDING, TOPOLOGY AND ELECTRON DISTRIBUTION

The boron hydrides and their derivatives have, by their very existence, contributed substantially to a better understanding of covalent bonding. This has come about as a direct result of the unusual structures which could not be accounted for on the basis of simple two-centre two-electron bonds. This difficulty gave rise to the generic term 'electron-deficient' compounds, since in general there are fewer electrons available for bonding than orbitals capable of being used in the bonding scheme. It should, however, be emphasized that the compounds are not strictly electron deficient in the chemical sense, since all the bonding orbitals are completely filled.



(62)

In simple covalent bonding theory, molecular orbitals are formed by the linear combination of atomic orbitals (L.C.A.O.); for example, two atomic orbitals can combine to give one bonding and one antibonding 'molecular orbital' and the orbital of lower energy (the bonding molecular orbital) will be occupied by a pair of electrons. This is a special case of a more general situation in which a number of atomic orbitals are combined together by the L.C.A.O. method to construct an equal number of molecular orbitals of varying energies, some of which may be bonding, some non-bonding and some antibonding. In this way, two-centre, three-centre and other multicentre orbitals may be envisaged.

As an example, we may choose the three types of three-centre bonds which find considerable application in the boron hydrides. The bonding of bridge hydrogens

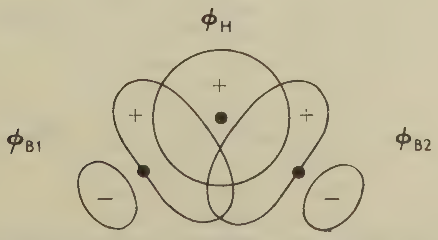


Fig. 3.1.—Overlap of atomic orbitals in bridge hydrogen bonding

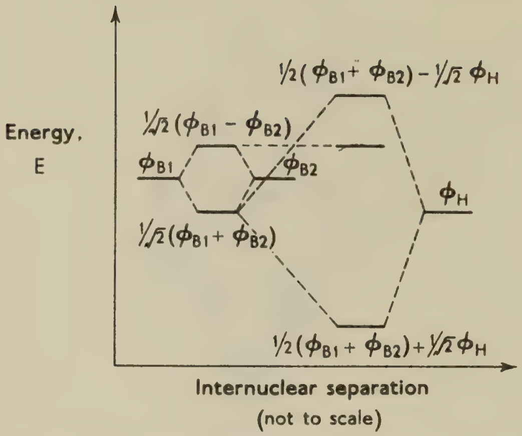

$\frac{1}{2}(\phi_{B1}+\phi_{B2})-\frac{1}{\sqrt{2}}\phi_H$
$\frac{1}{\sqrt{2}}(\phi_{B1}-\phi_{B2})$
Energy, E
ϕ_{B1}
ϕ_{B2}
ϕ_H
$\frac{1}{\sqrt{2}}(\phi_{B1}+\phi_{B2})$
$\frac{1}{2}(\phi_{B1}+\phi_{B2})+\frac{1}{\sqrt{2}}\phi_H$
Internuclear separation
(not to scale)

FIG. 3.2.—Energy correlation diagram for bridge hydrogen bonding

may be described in terms of linear combinations of two hybrid boron atomic orbitals ϕ_{B1}, ϕ_{B2} and the hydrogen orbital ϕ_H. The overlap of the orbitals to form a bonding molecular orbital is indicated in Fig. 3.1 and the energies of all three resulting molecular orbitals are diagrammatically represented by the energy correlation diagram (Fig. 3.2). The three normalized and orthogonal molecular orbitals ψ_1, ψ_2, and ψ_3 are given by the forms

$$\psi_1 = \tfrac{1}{2}(\phi_{B1}+\phi_{B2})+(1/\sqrt{2})\phi_H$$
$$\psi_2 = (1/\sqrt{2})(\phi_{B1}-\phi_{B2})$$
$$\psi_3 = \tfrac{1}{2}(\phi_{B1}+\phi_{B2})-(1/\sqrt{2})\phi_H$$

of which only ψ_1 is bonding.

Similarly, central three-centre bonding between three boron atoms each hybridized *sp*^{3} is described in terms of combinations of ϕ_{B1}, ϕ_{B2} and ϕ_{B3}, and the bonding overlap is indicated in Fig. 3.3. The energies are represented on the correlation diagram, Fig. 3.4. Thus

$$\psi_1 = (1/\sqrt{3})(\phi_{B1}+\phi_{B2}+\phi_{B3})$$
$$\psi_2 = (1/\sqrt{2})(\phi_{B1}-\phi_{B2})$$
$$\psi_3 = (1/\sqrt{6})(\phi_{B1}+\phi_{B2}-2\phi_{B3})$$

The choice of the unique boron orbital ϕ_{B3} depends on the geometry of the situation.

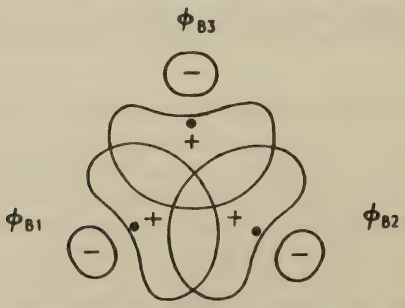


FIG. 3.3.—Overlap of atomic orbitals in central three-centre bonding

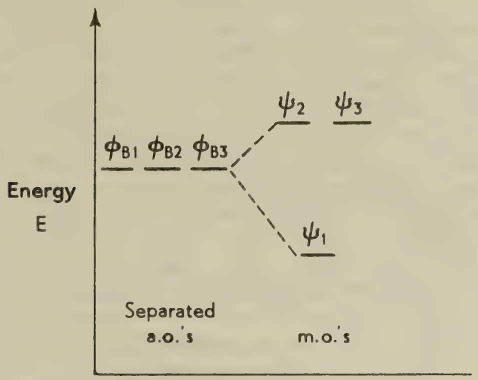


FIG. 3.4.—Energy correlation diagram for central three-centre bonding

Thus, for the open three-centre bond (Fig. 3.5), an essentially pure $2p$ orbital can be used, and the symmetry requirements now make the combinations:

$$\psi_1 = \tfrac{1}{2}[(\phi_{B1}-\phi_{B2})+(\sqrt{2})\phi_{B3}]$$
$$\psi_2 = (1/\sqrt{2})(\phi_{B1}+\phi_{B2})$$
$$\psi_3 = \tfrac{1}{2}[(\phi_{B1}-\phi_{B2})-(\sqrt{2})\phi_{B3}]$$

with the schematic energy correlation diagram, Fig. 3.6.

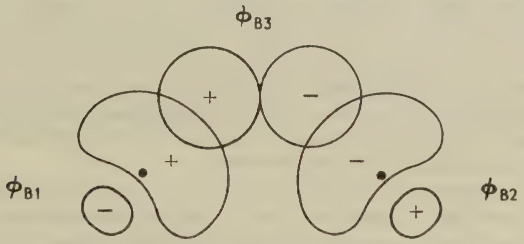


FIG. 3.5.—Overlap of atomic orbitals in open three-centre bonding

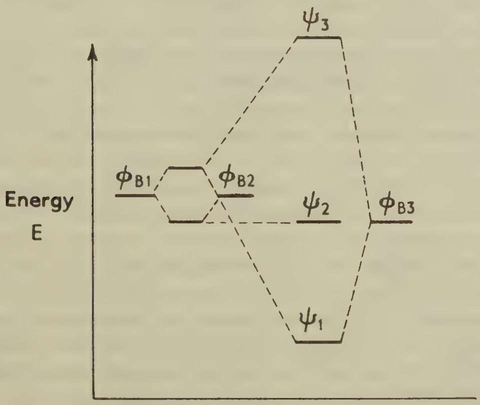


FIG. 3.6.—Energy correlation diagram for open three-centre bonding

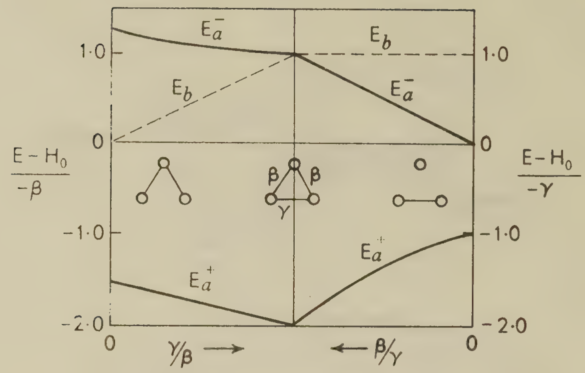


FIG. 3.7.—Results of the simplified L.C.A.O. method for three-centre bonds[22]

The results of the simplified L.C.A.O. method for three-centre bonds is shown in Fig. 3.7. Continuous variation from an open three-centre molecular orbital to a two-centre molecular orbital is depicted as a function of the ratios of the resonance integrals β and γ; β is the resonance integral between boron atoms 1 and 2 (or 2 and 3) and γ is the resonance integral between boron atoms 1 and 3. When the ratio $\gamma/\beta = 0$ the system corresponds to an open three-centre bond, when $\gamma/\beta = 1$ there is a central three-centre bond, and when $\beta/\gamma = 0$ the system corresponds to an ordinary two-centre electron-pair bond.

Any consideration of the bonding in the boron hydrides must logically start with diborane, for which the first satisfactory treatment was given by Longuet-Higgins[194, 194a, 195] who suggested that the orbitals on each of the two boron atoms are essentially sp^3 hybridized, and that two of these orbitals on each boron atom are used in the formation of the four terminal boron–hydrogen bonds. The remaining four boron orbitals, two hydrogen orbitals and four electrons are used in two sets to form the two boron–hydrogen–boron bridges (see Fig. 3). In each set, combination of two boron orbitals and one hydrogen orbital yields three molecular orbitals of which only one is strongly bonding. A number of more refined treatments of the diborane system have been made.[196–201, 201a,b]

The extension of the ideas of three-centre and multicentre bonding to the higher boron hydrides and their derivatives was a logical development; Lipscomb and his co-workers have been foremost in furthering these ideas.[22, 202] Two main approaches have been used to rationalize the structures. The first is essentially a valence-bond approach, based on localized two-centre and three-centre bonds, and finds its major application to species of relatively low symmetry. The second, more general molecular orbital approach is outlined on p. 268.

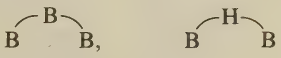
The simpler, valence-bond type approach has been developed by Lipscomb and co-workers[22, 203] to yield a topological theory which (a) describes the bonding in boron hydrides and derivatives of known geometry, and (b) predicts possible, but as yet unknown, boron hydrides and their derivatives which may be chemically feasible. The topological method relies for its success on the observation of gross similarities in structural features in known boron hydride species. For a species of any particular composition, all possible bonding schemes are obtained in terms of two- or three-centre orbitals, by arriving at a number of equations of balance which algebraically yield the number of B–H–B bridge bonds (s), the number of open or central three-centre BBB bonds (t), the number of B–B single bonds (y), and the number of BH_2 groups (x). All boron atoms are assumed to have at least one attached hydrogen atom and this is not separately specified. Certain of the bonding schemes are then rejected on the basis of geometrical considerations, or from the lack of precedent for certain interactions in known species. The resultant bonding structures can then be codified by the four numbers *styx*.

Charge distributions in boron hydride species can also be obtained on the basis of the two- and three-centre bond formalism. A zeroth approximation[202] may be made on the basis of a number of bonding schemes restricted to those which are the most symmetrical, or a better approximation[204] may be obtained from the relatively complete form of the three-centre formalism in which all resonance structures are written and a hybrid of these is taken as the basis for the charge distribution. As in any valence-bond method, there is the inherent uncertainty in allocating the coefficients of the different resonance and equivalent structures when determining the total wave function. Lipscomb[22] draws attention to the difference between resonance and equivalent structures; the former are a set of symmetry-equivalent structures having the molecular symmetry when considered as a group, and the latter are distinct ways of representing the arrangement of two-centre and three-centre bonds in the boron framework.

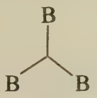
In representing the bonding arrangements in the boron hydride species, it has become conventional[22] to adopt the notation:

B—H, B—B

two-centre, two-electron bonds



open three-centre, two-electron bonds



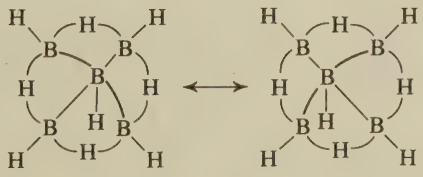
central three-centre, two-electron bond.

The most symmetrical bonding arrangements for known species containing five or more boron atoms are given below; the four numbers in parentheses indicate the values of the topological parameters *s*, *t*, *y* and *x*, as defined on p. 262. It will be noticed that there are always four lines (orbitals) emanating from or traversing each boron atom and one line emanating from or traversing each hydrogen atom. The valence structures have been discussed in refs. 22, 202, 205 or in the references indicated.

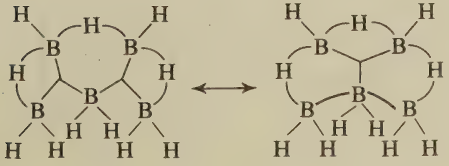
(a) *Hydrides*

Formula
(topology)

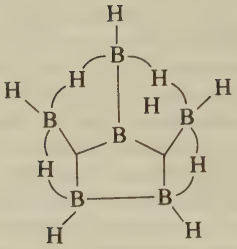
B_5H_9
(4,1,2,0)



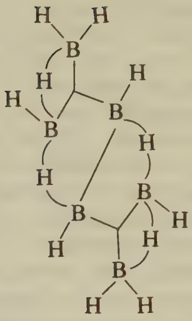
B_5H_{11}
(3,2,0,3)



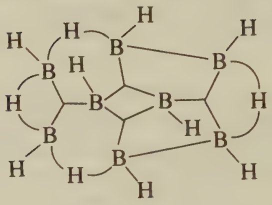
B_6H_{10}
(4,2,2,0)



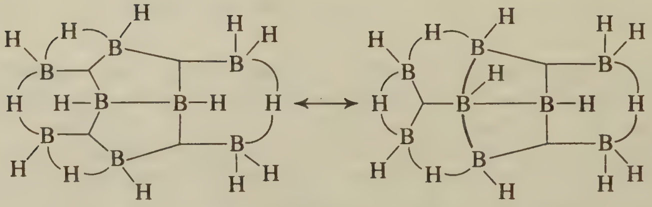
B_6H_{12}[126]
(4,2,1,2)



B_8H_{12}[129]
(4,4,2,0)

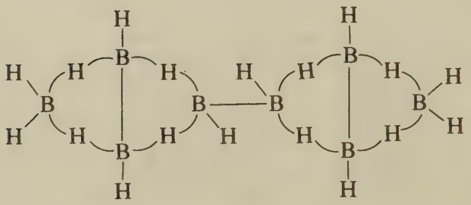


B_8H_{14} [132–3]
(4,4,1,2)

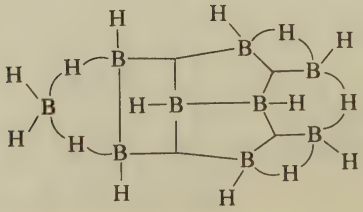


(This must be speculative until the structure is known.)

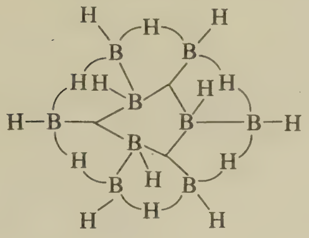
B_8H_{18}[135]
(8,0,3,2)



B_9H_{15} [139–41]
(5,4,2,1)

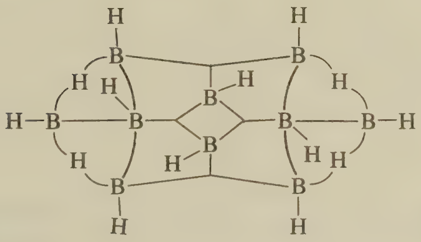


i-B_9H_{15}[142, 147]
(6,3,3,0)



(This structure, which must be speculative in view of the lack of experimental data, violates one of Lipscomb's topological rules.)

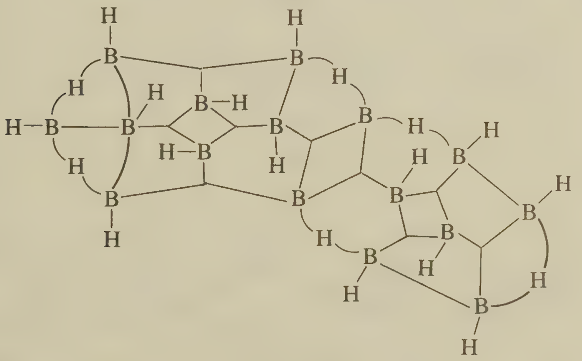
$B_{10}H_{14}$
(4,6,2,0)



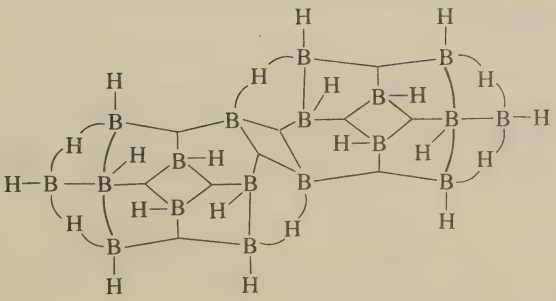
$B_{10}H_{16}$
(8,2,5,0)

This is simply two B_5H_8 units linked with a two-centre B–B bond through the apices. [See B_5H_9 (4,1,2,0).]

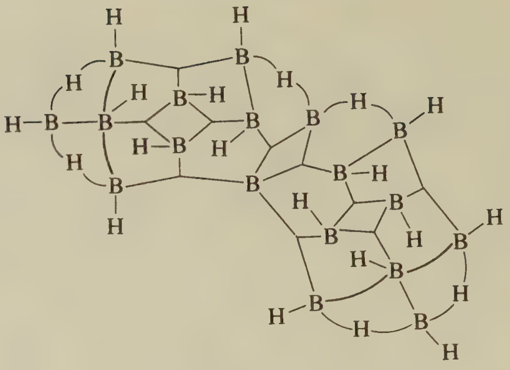
$B_{16}H_{20}$[176]
(6,10,4,0)



n-$B_{18}H_{22}$
(6,12,4,0)

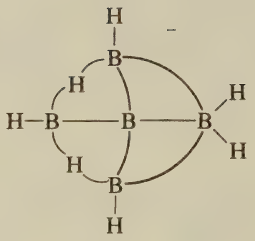


i-$B_{18}H_{22}$
(6,12,4,0)



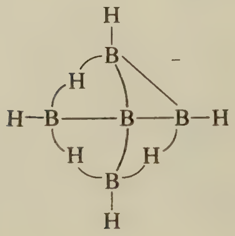
(b) *Hydride ions*

$B_5H_8^-$
(2,2,2,1)

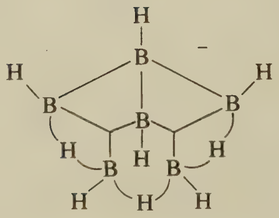


Known derivative,
$(Me_3NH)^+$ $[1\text{-}EtB_5H_7]^-$

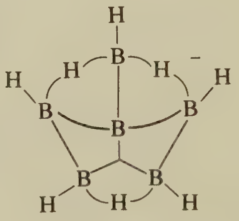
$B_5H_8^-$ [106]
(3,1,3,0)



$B_6H_9^-$ [117]
(3,2,3,0)

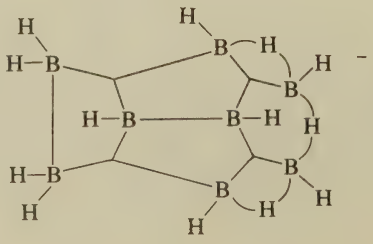


or



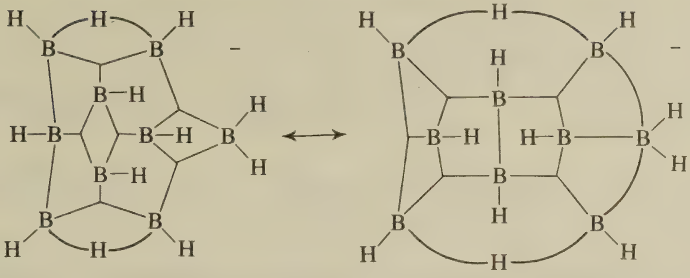
Other possible structures for $B_6H_9^-$ based on (2,3,2,1) and (1,4,1,2) topologies have been suggested.[22]

$B_8H_{13}^-$
(3,4,2,2)

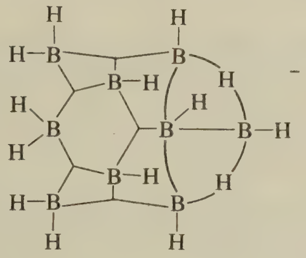


Known derivative
$EtNH_2,B_8H_{11}NHEt$

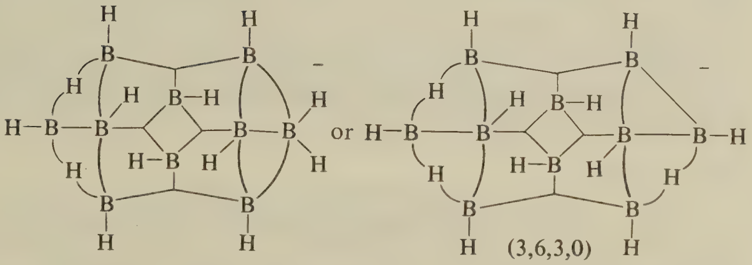
$B_9H_{12}^-$ [149]
(2,6,2,1)



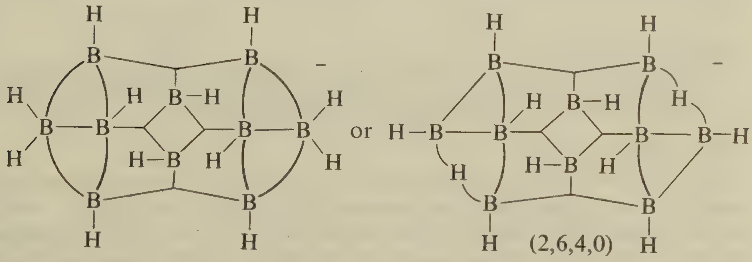
$B_9H_{14}^-$ [146]
(2,6,1,3)



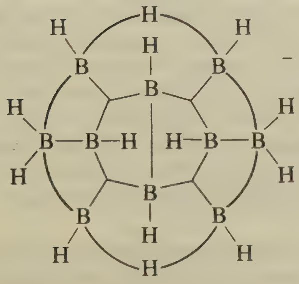
$B_{10}H_{13}^-$ [20,31]
(2,7,2,1)



$B_{10}H_{12}^{2-}$
(0,8,2,2)

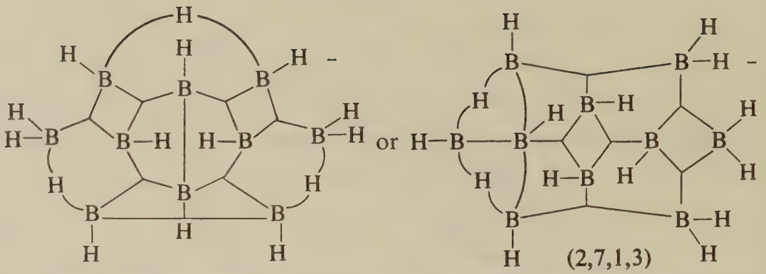


$B_{10}H_{14}^{2-}$ [162]
(2,6,3,2)



Other arrangements of (2,6,3,2) and also (4,4,5,0) topologies of $B_{10}H_{14}^{2-}$ have been described.[22]

$B_{10}H_{15}^-$ [149] (3,6,2,2)



Similar bonding structures can be written for the isoelectronic carborane species and their anions.

The second approach is that of the more rigorous molecular orbital method. With increasing complexity, or increasing symmetry in boron hydride species, the localized two- and three-centre bond approach, and even its valence-bond extensions become less adequate. This has been circumvented by the use of molecular orbital methods[204], and even approximate treatments can provide qualitative but nonetheless useful descriptions of highly symmetrical species. The basis of these methods has been discussed in detail by Lipscomb[22], and charge distributions, overlap populations and energies in many of the species have been obtained. In the most recent set of calculations on B_4H_{10}, B_5H_9 and B_5H_{11} the following generalizations were noted: (a) all atomic charges are less than $\pm e$; (b) apex borons are more negative than other borons; (c) borons in BH_2 groups are more positive than borons in BH groups; (d) all terminal hydrogens are negative and all bridge hydrogens are positive; (e) bridge hydrogens between BH_2 and BH groups are more strongly bonded towards the BH group; and (f) very low electron density exists directly between two boron atoms if these borons are joined by a bridge hydrogen[205*a*, *b*].

BORON HYDRIDES

The results of the molecular orbital method have been reported for pentaborane(9)[199, 204, 206–8, 208a,b,c], pentaborane(11)[204], hexaborane(10)[204], nonaborane(15)[204], decaborane(14)[170, 199, 204, 209, 210], and decaborane(16).[204, 207] In addition, calculations have been carried out for the substituted hydride, 2,4-di-iododecaborane.[211–13]

HYDRIDE ANIONS

Calculations have been carried out on the known hydride ions $B_3H_8^-$ [204], $B_9H_{14}^-$ [204], $B_{10}H_{14}^{2-}$ [204], $B_{10}H_{13}^-$ [214], and the hypothetical ions $B_4H_7^-$ [214–15], $B_5H_{10}^-$ [214], $B_6H_{11}^+$.[214–15]

POLYHEDRAL SPECIES

Calculations for polyhedral species are particularly significant, since the early calculations[216] predicted the existence of $B_{12}H_{12}^{2-}$ and $B_6H_6^{2-}$ well before their experimental discoveries. Programmes for L.C.A.O.–M.O. calculations for the known polyhedral borane anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ and the then hypothetical $B_5H_5^{2-}$ and $B_6H_6^{2-}$ anions have been developed[204, 217] using Slater orbitals, and the calculations compared with those derived from atomic self-consistent field (S.C.F.) functions.[217] Calculations on polyhedral systems, in particular the $B_{12}H_{12}^{2-}$ ion, have also been carried out using a crystal-field model[218], and it was found that the crystal-field energy levels were comparable with those from the L.C.A.O. molecular orbital method, and that discrepancies were reduced when the L.C.A.O. assumption that $\alpha(2s)=\alpha(2p)$ was modified by making $\alpha(2s)$ more negative. Calculations on the $B_7H_7^{2-}$ and $B_8H_8^{2-}$ systems have also been obtained by the Hoffmann and Lipscomb method.[42] Self-consistent field calculations on B_4H_4 have also been reported.[219]

In these calculations, the ground state of all these species is found to be the dinegative anion, although more approximate calculations involving only framework orbitals for the B_7 system yielded $B_7H_7^0$ as the ground state species. Throughout the Hoffmann and Lipscomb method of calculations on the polyhedral ions, a relatively large energy gap between the highest filled and lowest unfilled molecular orbitals is obtained.[26] This is consistent with the experimental observations of the u.v. spectra and polarographic data for the polyhedral anions.

CARBORANES

Population analyses of the L.C.A.O. molecular orbitals and charge distributions in all the geometrical isomers of the trigonal $B_3C_2H_5$, tetragonal $B_4C_2H_6$, pentagonal bipyramidal $B_5C_2H_7$ and icosahedral $B_{10}C_2H_{12}$ isomers have been computed, and predictions made of the reactivities of these compounds and their derivatives.[220] In addition, non-empirical S.C.F. methods have been developed and orbital charges for $B_{10}C_2H_{12}$ and its derivatives have been obtained.[74, 76, 199, 221]

The consequences of charge distribution on the chemical properties, and effects of sequential substitution in the polyhedral ions and carboranes have been examined, and predictions made.[74, 222–4] However, caution must be used in applying the results of charge density calculations, since the results necessarily apply only to the ground states of the species, and in addition consideration should be given to effects such as steric requirements, cooperative transition states and charge transfer effects of substituents on the particular species under consideration.

A different approach to predictions about boron hydrides depends on geometry for its success. It has been shown that H–H contacts in known boron hydrides are 'reasonable' ($\geqslant$about 2 Å) and only a few new boron hydrides based on a single icosahedral fragment are predicted.[225]

PART 4: PHYSICAL PROPERTIES OF THE BORON HYDRIDES

The general physical properties of the boron hydrides are summarized in the Tables below; spectroscopic properties are listed separately. Measured values of thermodynamic data are reported in the Tables; in addition a number of predictions of

A. Tables of Physical and Thermodynamic Data

Table 4.1.—Physical Properties of Pentaborane(9), B_5H_9

Physical property	Data or description	Ref.	Other refs.
Melting point	−46·0°C	231	232
Boiling point	60·0°C	233	232
Density	$0{\cdot}6404 - 0{\cdot}000883T$	234	231, 232, 235–8
Vapour pressure	$\log p_{\mathrm{mm}} = 5{\cdot}6352 - 1384/(T+250)$ (25–75°C)	233,	238, 240–1
	$\log p_{\mathrm{mm}} = 4{\cdot}4803 - 730/(T+160)$ (75–125°C)	239	
Critical point T_c	244°C	242	
P_c	557 p.s.i.a.	243	
Dipole moment	2·13 D (g), 3·4 D (l)	99	241
Dielectric constant	28 (0°C)	244	241
Refractive index	1·4445	245	
Surface tension	$\gamma = (71{\cdot}1 - 0{\cdot}143T)\alpha^{2/3}$ dynes cm^{-2}	246	
Viscosity (dynamic)	$\eta = 0{\cdot}4988$ poise (25°)	237	
(kinematic)	$\log \eta = (344{\cdot}75/T) - 1{\cdot}45851$ centistoke	234	
Thermal conductivity	$K_L = 0{\cdot}0874 - (6{\cdot}84 \times 10^{-5})t$ (B.Th.U./hr-sq. ft-°F/ft; t in °F)	247	
Other properties	The molecular volume of B_5H_9 has been reported.	248	
	The forced convection heat transfer characteristics have been described.	249	
	Some early data are to be found.	32, 246	

thermodynamic properties, heats of formation and bond energies of the boranes have been attempted.[226–8] In the Tables the most recent or most reliable data are presented, although references to other work are included.

No physical data are available for the hydrides B_8H_{12}, B_8H_{14}, B_8H_{18}, *i*-B_9H_{15} and *i*-$B_{18}H_{22}$.

In addition to the data in Table 4.2, a review of the thermodynamic properties of pentaborane(9) is available.[229] The solvent properties of pentaborane(9) were found to be similar to those of acetone, and the solubilities and conductivities of substituted ammonium iodides in pentaborane(9) were reported.[230]

Table 4.2.—Thermodynamic Properties of Pentaborane(9), B_5H_9

Property	Data	Ref.	Other refs.
ΔH_f°, kcal mole^{-1}	39·3 (g), 7·8 (l)	250	232, 245
	15·0±0·4	227	
ΔG_f°, kcal mole^{-1}	38·6 (l), 65·95 (g)	250	
Heat of formation from atoms, kcal mole^{-1}	1092·73	226	227
Heat of decomposition (kcal mole^{-1})	−9·9	227	
Heat of formation (kcal mole^{-1})	12·99±0·39	251	227
S° cal deg^{-1} mole^{-1}	44·16 (l), 23·53 (g)	250	
C_p° cal deg^{-1} mole^{-1}	19·0 (g), 35·8 (l)	252	
ΔH_{fusion} kcal mole^{-1}	1·466	253	
ΔS_{fusion} kcal mole^{-1}	6·457	24	
ΔH_{vap} kcal mole^{-1}	7·7	252	
ΔS_{vap} cal deg^{-1} mole^{-1}	23·3	252	

Table 4.3.—Physical Properties of Pentaborane(9D), B_5D_9

Physical property	Data	Ref.	Other refs.
Melting point	46·8°C	254	240
Vapour pressure	$\log p_{\text{mm}} = 7{\cdot}06325 - 1234{\cdot}857/[T+(-32{\cdot}259)]$ (240–333°K)	240	
Dipole moment	2·16 D	99	

Table 4.4.—Physical and Thermodynamic Properties of Pentaborane(11), B_5H_{11}

Property	Data	Ref.	Other refs.
Melting point	−122°C	255	231
Boiling point	65°C	231	256–7
Vapour pressure	$\log p_{\text{mm}} = 7{\cdot}8533 - 1675{\cdot}7/T$	258	256, 259
ΔH_f°, kcal mole^{-1}	16	260	232
	22·2±1	227	
ΔG_f° (298°), kcal mole^{-1}	48	260	232
S°, cal deg^{-1} mole^{-1}	70	260	
ΔS_{fusion}, cal deg^{-1} mole^{-1}	7·61	24	
ΔH_{vap}, kcal mole^{-1}	7·61	252	
ΔS_{vap}, cal deg^{-1} mole^{-1}	22·5	252	

Table 4.5.—Physical and Thermodynamic Properties of Hexaborane(10), B_6H_{10}

Property	Data	Ref.	Other refs.
Melting point	$-62{\cdot}3$°C	261	262–4
Boiling point	108°C	261	257, 263
Vapour pressure	$\log p_{mm} = 6{\cdot}4529 + 1{\cdot}75 \log T - 0{\cdot}00561T - 2270/T$	261	264
ΔH_f°, kcal mole^{-1}	17 $19{\cdot}6 \pm 2$	232 227	
ΔG_f° (298°), kcal mole^{-1}	45	260	
S° cal deg^{-1} mole^{-1}	69·6	260	

Table 4.6.—Physical and Thermodynamic Properties of Hexaborane(12), B_6H_{12}

Property	Data	Ref.	Other refs.
Melting point	-83°C	126	
Boiling point	Extrapn., 80–90°C	126	
Vapour pressure, mm	4·2 (-23°); 7·0 (-17°); 17 (0°)	126	
ΔH_f°, kcal mole^{-1}	14·7	232	126, 265

Table 4.7.—Physical Properties of Nonaborane(15), B_9H_{15}

Property	Data	Ref.	Other refs.
Melting point	$+2{\cdot}6$°C	261	131
Vapour pressure (mm)	0·8 (28°)	261	131

Table 4.8.—Physical Properties of Decaborane(14), $B_{10}H_{14}$

Property	Data	Ref.	Other refs.
Melting point	98·8°C	266–7	32, 252
Boiling point	213°C	266–7	32, 252
Density, g cm^{-3}	(l) 0·78 (100°), (s) 0·92 (99°)	32	268
Vapour pressure (solid)	$\log_{10} p_{mm} = 0{\cdot}013198T(°K) - 10{\cdot}577$	269, 270	271
Vapour pressure (liquid)	$\log_{10} p_{mm} = 4225{\cdot}345/T - 0{\cdot}0107975T + 16{\cdot}63911$	266, 269, 270	268, 271
Dipole moment	3·17 (CS_2) to 3·62 D (C_6H_6)	272–3	
Molar magnetic susceptibility	$(116 \pm 1{\cdot}5) \times 10^{-6}$	272	

Table 4.9.—Thermodynamic Properties of Decaborane(14), $B_{10}H_{14}$

Property	Data	Ref.	Other refs.
ΔH_f°, kcal mole^{-1}	26 (g), 8 (l), −16 (s)	232, 245, 252	227, 265–6, 274–5
ΔG_f° (298), kcal mole^{-1}	70 (g), 65 (s)	232	252, 266
S°, cal deg^{-1} mole^{-1}	83·8 (g), 42·48 (s)	232	266, 276
C_p°, cal deg^{-1} mole^{-1}	52·4 (s)	232	266, 277
ΔH_0°, kcal mole^{-1}	19·16±0·02	270	266
$\Delta H^\circ_{298(\mathrm{subl})}$, kcal mole^{-1}	18·33	270	266
$\Delta G^\circ_{298(\mathrm{subl})}$, kcal mole^{-1}	18·33	270	
$\Delta G^\circ_{298(\mathrm{vap})}$, kcal mole^{-1}	5·77	270	
$\Delta H_{\mathrm{fusion}}$, kcal mole^{-1}	7·8	252	
$\Delta S_{\mathrm{fusion}}$, cal deg^{-1} mole^{-1}	20·9	252	
ΔH_{vap}, kcal mole^{-1}	11·6	252	24
ΔS_{vap}, cal deg^{-1} mole^{-1}	31·1	252	24

In addition to the data in Tables 4.8 and 4.9, a review of the thermodynamic properties of decaborane(14) is available.[229] The adsorption of decaborane(14) on coconut charcoal has been found to be of the Langmuir type, and essentially independent of pressure.[269] The solubility of decaborane in a variety of solvents has been investigated; the room-temperature solubilities in g per 100 g of solvent are: ethyl acetate 50; *n*-propyl bromide 20; ethyl silicate 20; carbon disulphide 20; butyraldehyde 20; benzene 20; acetic anhydride 20; acetic acid 10–20; ethyl borate 10; carbon tetrachloride 10; caprylic acid 2–10; cyclohexane 4–5; *n*-heptane 2. It has been reported that decaborane mixtures with carbon tetrachloride are extremely shock-sensitive.[278]

Only fragmentary data have appeared for other boranes. The heat of formation of decaborane(16) is $\Delta H_f^\circ(298^\circ) = 34{\cdot}8$ kcal mole^{-1}.[246] The melting point of *n*-octadecaborane(22), $B_{18}H_{22}$, is 177–178·5°C[279] and that of icosaborane(16), $B_{20}H_{16}$, is 196–199°C[88]; the last compound sublimes (<1 mm Hg) at 100–120°C.[88]

In addition, the sorption properties of boron hydrides on zeolites have been described[280], and the gas–liquid chromatography of boron hydrides and their derivatives has been studied.[281–2] The neutron absorption properties of ^{10}B have been used to develop a slow-neutron scattering counter consisting of a powder (2·5:1) of ZnS(Ag):$B_{10}H_{14}$.[283]

B. Infra-red, Raman and Microwave Spectra of the Boron Hydrides

It is not intended in this section to present a detailed discussion of the spectra of the boron hydrides and their derivatives, since this aspect is covered in another section of this Supplement, and a number of reviews of the subject are available.[23–4]

An excellent list of references to published and less accessible work on the infra-red spectra of boranes and their derivatives is given in reference 24, and some representative spectra are presented in reference 23. In addition, the application of infra-red spectrometry in boron chemistry has been reviewed[284–5], and a more specialized study of the applications of matrix isolation methods to the boron hydrides is available.[286]

PENTABORANE(9)

A number of studies of the rotational and vibrational spectra of pentaborane(9) have been made. An analysis of the microwave spectra of B_5H_9 and B_5D_9 has yielded values for molecular dimensions and dipole moments.[98–9] The earliest study of the vibrational spectra was made by W. J. Taylor and co-workers[287] who reported the infra-red and Raman spectra of pentaborane(9). Some of these results were used in the more complete investigation of normal and deuterated pentaborane(9)[97], and an analysis was presented on the basis of a C_{4v} molecule. Further studies have led to a

Table 4.10.—*Infra-red and Raman Spectra (in cm^{-1}) of Pentaborane(9) Vapour*, B_5H_9*

I.R.	2610 (s), 2598 (s), 1844 (w), 1802 (m), 1621 (m)
Raman	2600 (vs), 2152 (P) (w), 2077 (P) (w), 1840 (P) (m)
I.R.	1449 (m), 1413 (m), 1126 (w)
Raman	1440 (vw), 1387 (vw), 1350 (vw), 1193 (P) (vw), 1170 (P) (vw), 1120 (P) (vw), 999 (P) (s)
I.R.	799 (w), 628 (s), 616 (s)
Raman	982 (P) (vs), 884 (w), 803 (P) (s), 793 (P) (s), 782 (m), 738 (m), 700 (m)
I.R.	605 (s), 568 (w)
Raman	606 (w), 596 (w), 566 (w)

* In this and subsequent Tables: P = polarized, s = strong, m = medium, w = weak, v = very.

reassignment of some of the frequencies[288], and group-theoretical reduction considerations of the overtone frequencies active in the near i.r. led to calculations of bond energies, bond distances and force constants for the B–H bonds.[289] Furthermore, a study of the Raman and infra-red spectra of deuterated pentaborane(9) led to frequency assignment and normal-coordinate analysis for the normal and deuterated molecule.[102] A theory for the determination of mean amplitudes of vibration in pyramidal XY_4 molecules has been applied to the skeletal vibrations of normal and deuterated pentaborane(9), and their mean amplitudes of vibration have been calculated at 0° and 298°K.[290]

The principal bands in the infra-red[128] and Raman[287] spectra of B_5H_9 are listed in Table 4.10. The corresponding spectrum of B_5D_9 vapour[97] is in Table 4.11.

PENTABORANE(11)

Work on the spectra of B_5H_{11} and B_5D_{11} has been directed mainly at identification, and assignments have been on the general basis of group frequencies.[128, 255, 291] The principal bands in the infra-red spectra of B_5H_{11} and B_5D_{11} are presented in Table 4.12.

HEXABORANE(10)

Several workers have studied the infra-red spectrum of hexaborane(10), but complete assignment has not been attempted.[128, 261, 264] The spectrum has been shown[264], and the principal bands[261] are listed in Table 4.13.

Table 4.11.—Infra-red Spectrum (in cm^{-1}) of B_5D_9 Vapour

2600 (w)	2520 (vw)	2370 (vw)	2235 (vw)	2180 (vw)	2100 (vw)
2005 (m)	1989 (m)	1972 (s)	1962 (s)	1780 (vw)	1520 (w)
1420 (w)	1397 (mw)	1386 (mw)	1377 (mw)	1347 (mw)	1342 (mw)
1338 (m)	1292–1300 (mw)		1230 (vw)	1198 (w)	1186 (w)
1180 (w)	1110 (w)	1068 (s)	1056 (s)	1046 (s)	972–980 (w)
968 (w)	964 (w)	960 (w)	946 (vw)	874 (vw)	856 (vw)
849 (w)	842 (w)	795 (w)	779 (m)	771 (m)	761 (s)
752 (s)	749 (s)	746 (s)	743 (s)	740 (s)	732 (m)
648 (w)	639 (w)	442 (m)	430 (m)		

Table 4.12.—Infra-red Spectra (in cm^{-1}) of B_5H_{11} and B_5D_{11}

B_5H_{11}	2548 (s)	2460 (s)	2312 (w)	2040 (m)	1940 (w)	1859 (w)		
B_5D_{11}	1960	1840		1515	1400			
B_5H_{11}	1435 (m)	1405 (m)	1164 (s)	1043 (m)	1020 (w)	951 (m)	899 (w)	703 (w)
B_5D_{11}	1090		850		1030	760	690	

Table 4.13.—Infra-red Spectrum (in cm^{-1}) of Hexaborane(10), B_6H_{10}

2610 (vs)	1940 (s)	1567 (wsh)	1547 (s)	1492 (sh)	1487 (sh)
1484 (vs)	1481 (sh)	1447 (sh)	1027 (sh)	1020 (w)	884 (s)
777 (sh)	760 (s)	752 (sh)	698 (sh)	690 (w)	668 (sh)

Table 4.14.—Infra-red Spectrum (in cm⁻¹) of Hexaborane(12), B_6H_{12}

2570 (vs)	2490 (s)	2308 (w)	1990 (m)	1930 (m)	1747 (w)
1627 (w)	1491 (s)	1393 (m)	1356 (m)	1164 (s)	1055 (s)
1023 (s)	942 (m)	891 (m)	883 (w)	755 (s)	747 (s)
702 (m)	682 (m)				

Table 4.15.—Infra-red Spectrum (in cm⁻¹) of Nonaborane(15), B_9H_{15}

2578	2428	2290	2132	2083	1942	1870
1832	1530	1440	1350	1275	1243	1225
1200	1160	1083	1058	1045	1014	962
940	898	856	830	787	743	728
710	690					

HEXABORANE(12)

The infra-red spectrum has been reported[126,128] although no detailed assignments have been given. The principal frequencies[128] are listed in Table 4.14.

NONABORANE(15)

The infra-red spectrum of nonaborane(15) has been recorded[261], but no detailed analysis reported. The principal bands are in Table 4.15.

DECABORANE(14)

A number of studies of the vibrational spectra of decaborane have been reported. The infra-red and Raman fundamental frequencies, together with molecular parameters, were used to calculate a value of 83·85 e.u. for S°_{298} of the gas, compared with a thermodynamic experimental value of 87·36 e.u.[258] The spectrum has been shown, and a number of the weak bands of the earlier investigations have been queried.[292] Other investigations have been made[293–4], and vapour, solution and solid spectra reported.[294] The effect of solvent on the B–H stretching frequency was correlated with an essentially non-polar B–H bond[295], and the general boron–hydrogen stretching and bonding assignments have been reviewed.[285] The principal bands in the vibrational spectra[276] are presented in Table 4.16.

DECABORANE(16)

The infra-red spectrum of decaborane(16) has been shown[175,296], and although accurate data are not available, it was found, as expected, to be similar to that of pentaborane(9).

n-OCTADECABORANE(22)

The infra-red spectrum of n-$B_{18}H_{22}$ was observed to contain bands attributable to terminal and bridging boron–hydrogen vibrations and complex framework vibrations.[279] The nujol mull spectrum[297] is presented in Table 4.17.

i-OCTADECABORANE(22)

The infra-red spectrum differs slightly from that of n-$B_{18}H_{22}$, and the nujol mull spectrum is given in Table 4.18[297].

ICOSABORANE(16)

The infra-red spectrum of $B_{20}H_{16}$ has been shown[88,89], and the principal bands are listed in Table 4.19.

Table 4.16.—Infra-red and Raman Spectra (in cm^{-1}) of Decaborane(14), $B_{10}H_{14}$

I.R. (solid)	2624 (s),	2613 (vs),	2594 (sh),	2578 (s),	2566 (vs),	2544 (s),	2532 (vs)		
I.R. (CS_2 soln)	2650 (s) ←			one strong band		→	2500 (s)		
Raman (CS_2 soln)	2600 (s) ←			one strong band		→	2550 (s)		
I.R. (Solid)	2280 (vw),	2245 (vw),	2190 (vw),	2140 (vw),	2085 (vw)		2020 (vw),	1990 (vw),	1950 (w)
I.R. (CS_2 soln)	2290 (vw),		2200 (vw),	2145 (vw),	2080 (vw),	2040 (vw),		2000 (vw),	1950 (w)
Raman									1946 (w)
I.R. (Solid)		1900 (m),	1875 (s),		1795 (m),		1720 (vw),	1700 (vw),	1665 (m)
IR (CS_2 soln)	1925 (m),		1890 (m),	1820 (w),	1790 (vw),	1745 (vw),		1700 (vw),	1675 (w)
Raman			1880 (w)						
I.R. (Solid)	1625 (m),	1590 (s),	1570 (vs),	1550 (s),	1490 (m),	1450 (m),	1415 (m),	1390 (m)	
I.R. (CS_2 soln)	1625 (w) ←			CS_2		→	1415 (m)		
Raman									
I.R. (Solid)	1360 (m),	1300 (vw),	1265 (vw),	1250 (vw),	1210 (vw),	1190 (vw),	1160 (vw),	1145 (vw),	1100 (m)
I.R. (CS_2 soln)	1355 (w),		1265 (vw),	1250 (vw),	1210 (vw),		1170 (vw),	1152 (vw),	1110 (w)
Raman									
I.R. (Solid)	1058 (w),	1035 (m),	1003 (m),	968 (m),	961 (m),	954 (m),	943 (m),	938 (s)	
I.R. (CS_2 soln)	1065 (w),	1042 (vw),	1009 (vs),		960 (m),	955 (w),		932 (s)	
Raman	1060 (vw),	1040 (vw),	1005 (w),		960 (w)				
I.R. (Solid)	920 (vs),	915 (s),	901 (m),	858 (vw),	823 (s),	816 (vs),	775 (m),	765 (sh),	752 (s)
I.R. (CS_2 soln)	918 (s),		896 (m),	856 (m),	817 (m),	808 (s),		766 (s)	
Raman	921 (w),		901 (w),	858 (s),				763 (w)	
I.R. (Solid)	744 (m),	718 (s),	712 (vs),	701 (m),	690 (m),	649 (m),	635 (m)		
I.R. (CS_2 soln)	740 (w),	716 (vs),		701 (m),		643 (w),			
Raman			709 (s),					588 (w),	508 (w)
I.R. (Solid)	461 (w),	446 (w)							
I.R. (CS_2 soln)									
Raman	456 (m),		424 (vw),	350 (s),	295 (w),	230 (m)			

Table 4.17.—Infra-red Spectrum (in cm^{-1}) of n-Octadecaborane(22), n-$B_{18}H_{22}$

2550 (s)	1940 (w)	1390 (w)	1200 (w)	1080 (m)
990 (s)	950 (sh)	945 (m)	925 (s)	910 (s)
878 (w)	835 (s)	805 (w)	782 (m)	760 (m)
738 (m)	725 (m)	712 (m)	695 (m)	668 (w)

Table 4.18.—Infra-red Spectrum (in cm^{-1}) of i-Octadecaborane(22), i-$B_{18}H_{22}$

2550 (s)	1940 (w)	1220 (w)	1152 (w)	1080 (w)	1030 (w)
1000 (s)	970 (w)	950 (m)	935 (w)	920 (w)	910 (w)
860 (m)	833 (m)	792 (w)	780 (w)	769 (w)	743 (m)
728 (w)	711 (w)	695 (w)	660 (m)	638 (w)	

Table 4.19.—Infra-red spectrum (in cm^{-1}) of Icosaborane(16), $B_{20}H_{16}$

2600 (s)	2570 (sh)	960 (s)	915 (w)	890 (w)
870 (m)	840 (w)	790 (m)	765 (w)	720 (s) triplet

C. Nuclear Magnetic Resonance Spectra of the Boron Hydrides

Much work has been published on the n.m.r. spectra of the boranes and their derivatives. The earliest application of the technique was reported by Kelly et al.[298], and the application of double resonance techniques was reported in the early work.[299, 300] There are several compilations of data available in the literature.[22, 26, 301–6] Much of the useful structural information has come from examination of the ^{11}B resonances, and the early data were obtained on instruments operating at around 12·3 MHz. With the increasing availability of high resolution instruments operating at higher magnetic field strengths, many of the more recent data have been obtained at around 19·3 MHz, and even better information is now being obtained from instruments operating around 32 MHz, which is probably about the ultimate frequency obtainable with instruments using conventional electromagnets or permanent magnets. A few spectra have also been obtained at 64·2 MHz using superconducting magnets operating at liquid helium temperature.

Proton spectra are often much less informative structurally unless spin decoupling facilities are available. This is due to the inherently broad lines arising from the quadrupole relaxation induced by coupling of the protons to the ^{11}B and ^{10}B nuclei, and to the large multiplicity of lines arising from the same cause (the nuclear spin quantum number of ^{11}B is $\frac{3}{2}$, and that of ^{10}B is 3, leading to quartets and septets respectively).

The parameters for the boron hydrides are given in Table 4.20.

The observed anomalies in the n.m.r. spectra of some of the boron hydrides and their derivatives, namely B_5H_{11} and B_6H_{10}, have been discussed in terms of rapidly tautomerizing structures.[314] A possible approach to the theoretical calculation of n.m.r. parameters in the boron hydrides has been mentioned[315], and ^{11}B shifts correlated with ring-current effects.[316] A possible route to decoupled spectra by using the interaction with paramagnetic species has been described[317], in addition to elucidation of ^{11}B n.m.r. spectra by heteronuclear spin decoupling.[318]

Two excellent reviews of the n.m.r. spectra of a variety of boron hydride derivatives have recently appeared[26, 306] and a correlation of boron hydride spectra has been presented.[319] Certain very tentative 'rules' are beginning to emerge though these should be used with considerable caution, e.g.

Table 4.20.—^{11}B *n.m.r. Spectra of the Boron Hydrides*

Compound	Position or data	δ (ppm)*	J (Hz)	Reference, comments
B_5H_9	apex	+70·0 (+69·6)	173 (170)	300, 301–2
	base	+30·6 (+30·8)	160 (168)	
B_5H_{11}	apex	+71·7	(170) 168	300, 307–8
	base BH	+20·5 est	162	
	base BH_2	+15·3 est	132	
B_6H_{10}	apex	+69·4	182	309
		+ 3·2	160	
B_6H_{12}	BH	+42·9	158	126
	BH_2	+ 8·3	129	
	BH	− 5·3	160	
B_8H_{12}	doublet not assigned	+14·8	169	diethyl ether
	doublet not assigned	+38·2	141	133
	doublet not assigned	+11·4	168	pentane
	doublet not assigned	+38·7	153	133
B_8H_{14}	doublet	− 5·9	161	133
	doublet	+39·6	153	
	doublet	+57·1	154	
B_8H_{18}	doublet	+59·1	148	135
	doublet	+21·9	122	
	triplet	+25·3	124	
B_9H_{15}	complex spectrum at 12·8 MHz	+72·7		261
		+61·0		
		+46·4		
		+20·7		
		+ 9·7		
		− 1·8		
i-B_9H_{15}	broad doublet	+23·2	136	143
	doublet	+49·2	163	
	doublet	+62·2	163	
$B_{10}H_{14}$	2,4	+53·6 +54·0	162	310, 311–12
	5,7,8,10	+17·5	157	313–14
	6,9	+ 8·5	152	
	1,3	+ 6·9		
$B_{10}H_{16}$	spectrum consists of high field singlet low field doublet			22
$B_{18}H_{22}$	complex spectrum at 19·3 MHz	+42·5		22, 297
		+33·7		
		+24·9		
		+13·5		
		+ 5·2		
		− 0·5		
		− 7·8		
		−11·3		
		−21·2		
i-$B_{18}H_{22}$	complex spectrum at 19·3 MHz	+43·5		22, 297
		+35·7		
		+32·1		
		+22·3		
		+19·7		
		+11·4		
		+ 2·3		
		− 6·7		
		− 9·6		
		−16·6		
$B_{20}H_{16}$	peaks at 19·2 MHz	+27·4		88–9
		+18·5		
		+ 7·8		
	on ^{1}H saturation	+22·4		
		+15·6		
		+ 7·8		

* Chemical shifts are quoted relative to $B(OMe)_3$; to obtain shifts relative to BF_3,OEt_2 subtract 18·2.

(i) other things being equal, the boron resonance occurs at higher field the greater the electron density on B; (note however that 'other things' are rarely equal, see especially (ii) below);

(ii) most chemical shifts are probably explicable on the basis of a difference primarily in the paramagnetic shielding of boron atoms in differing chemical environments;

(iii) proton resonances generally (but not invariably) occur in the same order with increasing field strength as do the resonances of the boron atoms to which the hydrogen atoms are bonded;

(iv) bridge-proton resonances usually occur at higher field than do the resonances of other hydrogen atoms attached to boron in the same molecule;

(v) the frequently invoked rule that 'apex boron resonances occur at low field' is not valid as a generalization;

(vi) substitution for hydrogen on a boron atom, in addition to shifting the resonance of the substituted boron atom, often shifts other boron resonances as much or even more and the shifts may be in the same or in the opposite direction, according to the substituent.

Specific n.m.r. studies on boron hydride derivatives include the structures of B_5H_8I[320], B_5H_8Br[320–1] and $B_{10}H_{13}I$.[320, 322–3] Two isomers of $B_{10}H_{13}Cl$ have been identified as 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$.[324] The n.m.r. spectra of $B_{10}H_{12}(Ligand)_2$ compounds have been the subject of two investigations[325–6], and complete assignment of the ^{11}B n.m.r. of a series of these compounds has been obtained.[326] N.m.r. studies of boron complexes[327], ethylated pentaboranes and decaboranes, and perchloro cage-compounds[329] have also been reported. A complete listing of all n.m.r. data on the boranes and their derivatives up to 1968 together with a full discussion of the spectra and their implications has recently been published.[26]

D. Electronic Spectra of the Boron Hydrides

Little work has been reported on the electronic spectra of most of the boranes. The u.v. spectrum of B_5H_9 was found to be a featureless continuum.[330] The spectrum of decaborane has been recorded, and is found to absorb strongly in the u.v. at 265 nm.[331–2] The u.v. spectra of gaseous $B_{10}H_{14}$, of its solutions in cyclohexane and acetonitrile, and of crystalline $B_{10}H_{14}$ have been obtained; that of the crystal was polarized perpendicular to the two-fold axis of the molecule (crystal *c*-axis). A blue shift in the polar solvent acetonitrile indicated that the dipole moment in the excited state was less than that in the ground state.[333]

The u.v. spectrum of *n*-$B_{18}H_{22}$ showed three absorptions with λ_{max}nm(ϵ_{max}) : 332 (6560), 273·5 (3560), and 217 (15,900).[279] $B_{20}H_{26}$ showed only end absorption beginning at 350 nm.[89]

E. Mass Spectra of Boron Hydrides

The mass spectra of most of the boron hydrides have been reported. Mass spectral evidence has been cited for the existence of a number of hydrides which have otherwise been uncharacterized, including several heptaboranes (for which this evidence has been questioned), $B_{11}H_{17}$, $B_{14}H_{22}$, $B_{15}H_{21}$ and $B_{20}H_{26}$. Under normal conditions misleading information can be obtained through pyrolysis of the material in the ion source, and care must be used in the interpretation of fragmentation data. A number of general papers contain fragmentation data for the common hydrides.[334–9]

A general feature of all mass spectra from the higher boranes is the presence of groups of peaks reflecting the various possible isotopic abundances of ^{10}B and ^{11}B in particular molecules as modified by removal of successive hydrogen atoms from the various species. The situation has recently been reviewed.[338] For boron with normal isotopic abundance ($^{11}B/^{10}B \simeq 4{\cdot}0$) the abundance ratios of all the isotopic species in a particular ion group are readily calculated by simple statistics. Thus, for any species containing $x+y$ boron atoms the concentration of any species $^{11}B_x{}^{10}B_y$ is given by

$$[^{11}B_x{}^{10}B_y] = \frac{(x+y)!}{x!y!}(0\cdot80)^x(0\cdot20)^y$$

The values of the statistical weight factor $(x+y)!/(x!y!)$ are simply values of the binomial coefficients. For example, for a species with five boron atoms the concentrations of the various isotopic variants and their abundance ratios relative to $^{11}B_5$ are as follows:

Isotopic species	*Concentration*	*Abundance ratio*
$^{11}B_5$	$1\ (0\cdot80)^5$	1·0
$^{11}B_4^{10}B$	$5\ (0\cdot80)^4(0\cdot20)$	$5/4 = 1\cdot25$
$^{11}B_3^{10}B_2$	$10\ (0\cdot80)^3(0\cdot20)^2$	$10/4^2 = 0\cdot625$
$^{11}B_2^{10}B_3$	$10\ (0\cdot80)^2(0\cdot20)^3$	$10/4^3 = 0\cdot156$
$^{11}B^{10}B_4$	$5\ (0\cdot80)(0\cdot20)^4$	$5/4^4 = 0\cdot0195$
$^{10}B_5$	$1\ (0\cdot20)^5$	$1/4^5 = 0\cdot00098$

This distribution is shown on the left-hand side of Fig. 4.1. The observed mass spectrum of B_5H_9, for example, will differ somewhat from this because of successive abstraction of hydrogen atoms; the actual spectrum observed depends on the operating conditions (temperature, ionizing voltage, etc.) but a typical spectrum[339] is shown on the right-hand side of Fig. 4.1.

Similar calculations have been carried out for other boranes and the results are given in Table 4.21; the values for B_5 corresponding to those above are boxed-in along the B_5 diagonal for illustration. Typical mass spectra are shown in Fig. 4.2 for eight common boranes. The individual boranes will now be considered separately.

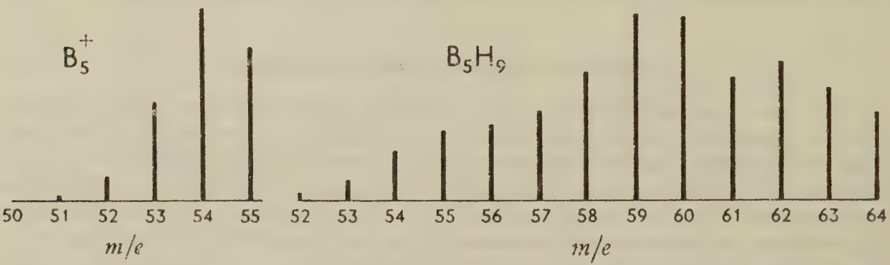


FIG. 4.1.—Calculated mass spectrum for B_5^+ and observed mass spectrum for B_5H_9, both with normal $^{11}B/^{10}B$ isotopic abundance ratio

Table 4.21.—Normal Statistical Distribution of Boron Isotopes (80% ^{11}B, 20% ^{10}B) in a $^{10}B_x^{11}B_y$ System where $x+y$ varies from 1 to 10

	$^{10}B_0$	$^{10}B_1$	$^{10}B_2$	$^{10}B_3$	$^{10}B_4$	$^{10}B_5$	$^{10}B_6$	$^{10}B_7$	$^{10}B_8$	$^{10}B_9$	$^{10}B_{10}$
$^{11}B_0$	—	20·0	4·0	0·8	0·16	0·03	6×10^{-3}	1×10^{-3}	3×10^{-4}	5×10^{-5}	1×10^{-5}
$^{11}B_1$	80·0	32·0	9·6	2·56	0·60	0·15	0·04	8×10^{-3}	2×10^{-3}	4×10^{-4}	
$^{11}B_2$	64·0	38·4	15·4	5·1	1·54	0·43	0·11	0·03	7×10^{-3}		
$^{11}B_3$	51·2	41·0	20·5	8·2	2·9	0·92	0·28	0·08			
$^{11}B_4$	41·0	41·0	24·5	11·5	4·6	1·7	0·55				
$^{11}B_5$	32·8	39·2	27·5	14·7	6·6	2·6					
$^{11}B_6$	26·2	36·7	29·4	17·6	8·8						
$^{11}B_7$	21·0	33·6	30·2	20·1							
$^{11}B_8$	16·8	30·2	30·2								
$^{11}B_9$	13·4	26·8									
$^{11}B_{10}$	10·7										

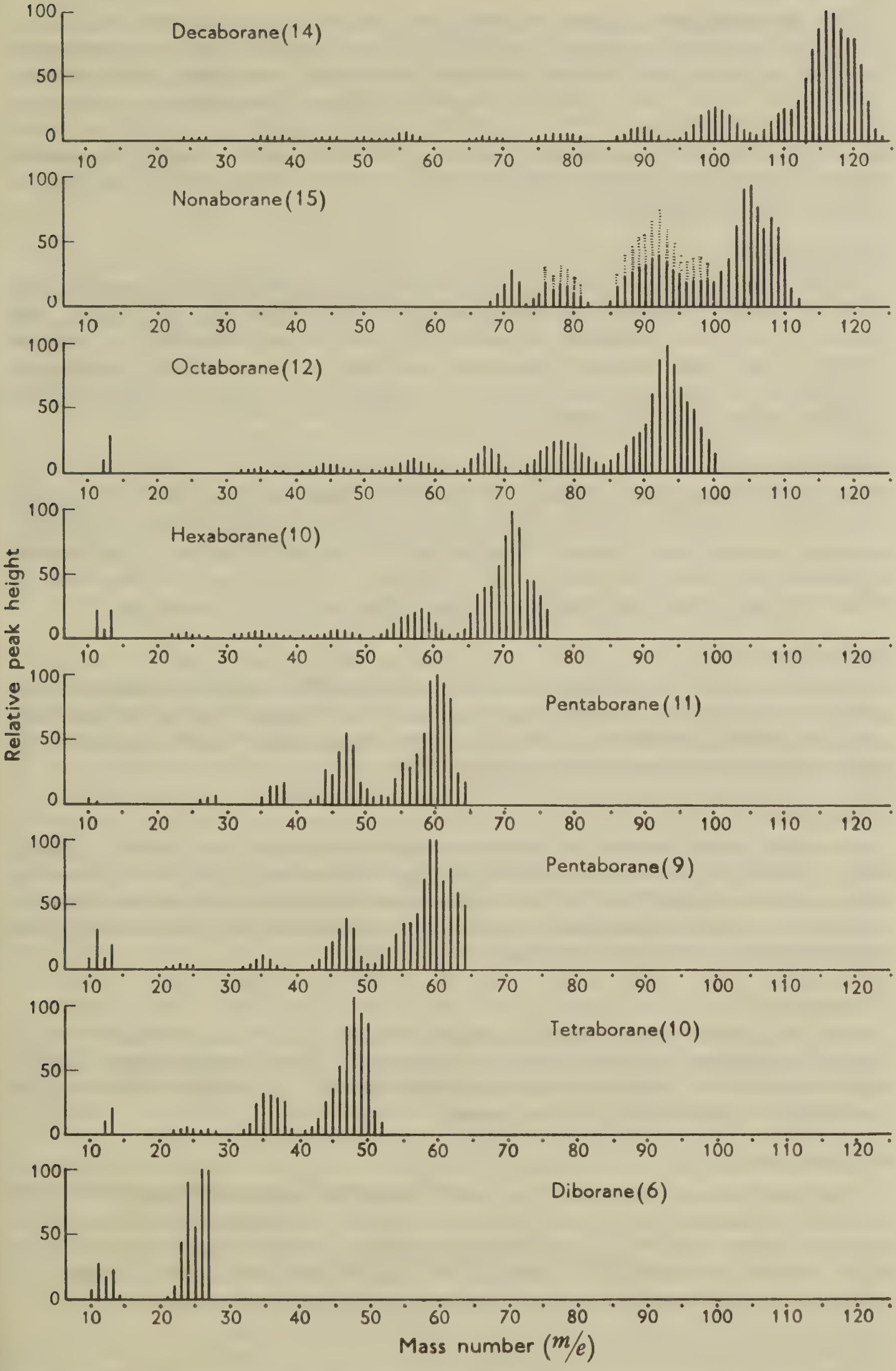


FIG. 4.2.—Mass spectra of boron hydrides

PENTABORANE(9)

Mass spectral data on pentaborane(9) may be found in references 240, 334–5. Studies of isotopically normal B_5H_9[334–5, 340] have yielded crude fragmentation patterns, and these together with studies of isotopically substituted species such as $^{11}B_5H_9$ and $^{11}B_5D_9$[342] have given monoisotopic fragmentation patterns. Appearance potential measurements[336, 342–5] on selected ions and studies of metastable transitions have been used to calculate ionization potentials and heats of formation of various fragment ions, and the results have been used in determining the decomposition path of the parent ion.

PENTABORANE(11)

Data for the mass spectrum of B_5H_{11}[128, 336, 346], including the polyisotopic spectrum, its reduced monoisotopic fragmentation, and similar data on $^{11}B_5H_{11}$ and $^{11}B_5D_{11}$, have been obtained. Appearance potential measurements on selected fragments, and observation of metastable ions have led to a suggested mechanism of fragmentation of the parent ion, and to calculations of heats of formation and ionization potentials of fragment ions.

HEXABORANE(10)

The polyisotopic mass spectrum of B_6H_{10} has been obtained[128, 263–4], and that at 11 eV has been reduced to a monoisotopic fragmentation pattern. The $^{11}B_6H_{10}$ spectrum has also been obtained, together with appearance potential measurements of selected fragments and metastable transitions, and the data have been used to obtain ionization potentials and the fragmentation path of the parent ion.[336]

HEXABORANE(12)

The polyisotopic mass spectrum of B_6H_{12} at 11 and 70 eV and the reduced monoisotopic spectrum at 11 eV have been described[128], although it had earlier been suggested as one product of an electric discharge through B_2H_6[347], and as a product of the pyrolysis of diborane in a shock tube.[348–9]

HEPTABORANES

A number of papers have appeared in which the hydrides B_7H_{11}, B_7H_{12}, B_7H_{13}, B_7H_{14}, and B_7H_{15} have been 'identified' by their mass spectra.[347–52] However, more recent work by Ditter and co-workers has indicated that these are probably spurious, and the fragmentation patterns are best accounted for in terms of alkylated or alkoxylated boranes or carboranes.[131]

OCTABORANE(12)

The polyisotopic fragmentation pattern of B_8H_{12} has been obtained[130–1], although no attempt has been made to reduce this to the monoisotopic species. Early reports[334, 353] were probably substantially correct, although the data were undoubtedly obtained on impure compounds.

NONABORANE(15)

Mass spectroscopic data were first used to show the existence of B_9H_{15}[350, 353, 354], although the spectra were almost certainly obtained with impure compounds. Even the more recent work[261, 355] has been questioned[131] and the fragmentation of pure B_9H_{15} shown to be difficult to obtain. No attempt has been made to reduce the polyisotopic fragmentation data to those of the monoisotopic species.

DECABORANE(14)

A number of investigations of the mass spectra of decaborane(14) have been made.[335, 340] In addition, appearance potential measurements on selected fragments of $^{11}B_{10}H_{14}$ and isotopically normal $B_{10}H_{14}$ have been made to obtain ionization potential data.[345, 356–8]

DECABORANE(16)

$B_{10}H_{16}$ was identified in the products of deuteron-irradiation of pentaborane(9)[189, 359], and ionization and appearance potentials, and a monoisotopic fragmentation pattern have been determined.[360-1] The B–B bond-dissociation energy for the apex-apex bond was found to be $3{\cdot}2 \pm 0{\cdot}2$ eV.[360]

HIGHER BORANES

Hall and Koski have obtained mass spectral data consistent with $B_{11}H_{17}$ from neutron irradiation of hexaborane(10) and pentaborane(9), and data indicating $B_{14}H_{22}$ and $B_{15}H_{21}$ have been obtained from irradiation of mixtures of boron hydrides.[189] The polyisotopic spectrum of $B_{20}H_{16}$ has been briefly mentioned.[88-9] Deuteron irradiation of decaborane(14) has led to the identification of $B_{20}H_{26}$ by mass spectrometry.[189]

OTHER STUDIES

The negative-ion mass spectra of some boron hydrides has been mentioned.[362] The reaction of noble gas ions with pentaborane(9) has been studied in a two-stage mass spectrometer.[363] The fragmentation of the pentaborane varied markedly as a function of the recombination energy of the noble gas ion, and breakdown curves for pentaborane(9) were constructed by plotting the relative abundances of products as a function of the excitation energy of the noble gas ions.

PART 5: PREPARATIONS OF THE BORON HYDRIDES

Before 1948, the preparation of the higher boranes was restricted to the somewhat crude methods of 'classical' hydrolysis of certain metal borides and pyrolysis of the lower hydrides, diborane and tetraborane. These methods suffered the great disadvantages of producing a rather restricted range of the more stable hydrides, and of being relatively non-specific methods, producing gross mixtures requiring extensive separations and purifications. Since 1948[364-5] and particularly since the advent of practical methods for producing diborane and tetrahydroborates in quantity, the pyrolytic method of producing the higher boranes has been developed remarkably so that techniques are now available for producing individual boranes in good yields. During the course of the surge of interest in boron hydride chemistry, which was brought about principally by the high-energy fuels programme in the U.S.A., plant was erected, and later dismantled, to produce decaborane(14) on the multi-ton per day scale by pyrolytic methods. The experimental results of pyrolysis studies are summarized in subsection B and the mechanisms discussed in subsection F. Other methods which are finding increasing applicability, particularly for the less stable boron hydrides, involve the protonation of hydride anions, and the catalytic chemical conversions of the boranes using, for example, a variety of Lewis bases. In addition, a number of lesser-known boranes have been produced in small quantities by electrical discharge methods involving other boron hydrides, and by radiation-induced reactions of boron hydrides, although both of these methods suffer the inherent disadvantage of non-specificity.

A. Classical Hydrolysis of a Boride

The classical method of preparing boron hydrides involved the hydrolysis of magnesium or beryllium boride with an acid such as hydrochloric or polyphosphoric acid.[32, 366] By this method, Stock was able to detect small quantities of B_5H_9, B_6H_{10} and $B_{10}H_{14}$ in the hydrolysis products, although the major volatile product was B_4H_{10}. Recent work[367] has suggested that the yields of hexaborane(10) were higher than those reported in the early literature.[32, 368] Other workers have described high yields of B_2H_6 and B_4H_{10}, with smaller amounts of B_5H_9, B_5H_{11} and B_6H_{10}.[369]

B. Pyrolytic Methods

PENTABORANE(9)

Stock originally reported the preparation of small quantities of B_5H_9 by pyrolysis of diborane or tetraborane.[32] The conversion of pentaborane(11) in the presence of hydrogen, or mixed boranes and hydrogen, to pentaborane(9) by prolonged heating at 120° in the presence of BCl_3 was described by Burg and Schlesinger.[258] Stock later reported that circulation of diborane at 120 mm initial pressure through a 250°C reactor for 4 h gave a yield of 56%.[370] A later attempt to develop a circulatory method involving pyrolysis at 120° to minimize undesirable solid products was not entirely satisfactory.[371] Diborane mixed with 5 volumes of hydrogen and pyrolyzed at less than 1 atm for 3 s at 250°, or up to 15 s at 225°, in a single pass through a furnace converted 25–30% of the diborane to pentaborane(9) in 60–70% yields[372], and thermal soaking could be used to obtain a 99% pure product.[373] Pre-pilot-plant[374] and pilot-plant[375–6] production by this method has been described. Similar methods have been described by other workers.[377–8] A three-stage hot–cold reactor has been reported to produce 80% yields of pentaborane(9).[379, 380] The pyrolysis of diborane by an adiabatic compression method was given a preliminary examination[381–3] and later extended[384–5], and pre-pilot-plant[386] and pilot-plant[387] preparations have been described. Gas-phase pyrolysis methods on a laboratory scale have been studied[378, 388–9] and attempts made to optimize conditions.[390] Other industrial studies of this method have been reported.[391–3] A method of gas-phase pyrolysis with liquid quench has been mentioned.[394] Pyrolysis methods involving liquid media or solvents have been investigated for the application of inert heat-transfer agents, inert or complexing solvents, and solvents to remove reaction products from gas-phase reactions.[378, 382, 395] The solvent or liquid medium was cyclohexane[396–7], heptane[398–9], or benzene[391–2], and pilot-plant production has been investigated.[400, 401] Some of this work has been reviewed.[402]

Pentaborane(9) has been purified by fractionally distilling tetraborane at reduced temperature and pressure, applying thermal treatment to remove remaining impurities, and distilling[403], and by distillation in the presence of a Lewis acid.[404] Its thermal stability at 100°, 125° and 150° has also been determined from the rate of pressure increase in 800 ml cylinders.[405] The reported reduction of a boron halide or an alkyl borate with hot atomized metal in the presence of hydrogen to produce some B_5H_9 is almost certainly the result of diborane pyrolysis.[406, 364]

PENTABORANE(11)

B_5H_{11} was discovered in 1924 after diborane had been stored at room temperature at slightly under 1 atm pressure.[32] The pyrolysis of diborane in a flow system at 100–120° for 2 min gave better yields of pentaborane(11)[258], and a purer product was obtained in a redesigned apparatus.[407] Other studies on diborane pyrolysis have been made.[408–9] 80–85% yields have been obtained in a flow system[410], and the effect of temperature indicated the highest yields of pentaborane(11) in a hot-tube reactor at 150–160°.[394] Small amounts of hydrogen favoured the production of pentaborane(11).[400] 74·5% yields have been obtained by pyrolysis of diborane over a zirconium boride catalyst.[411–12] The pyrolysis of tetraborane or diborane–tetraborane mixtures has also been used to prepare pentaborane(11).[413] 70% yields have been obtained in a hot–cold reactor consisting of concentric test-tubes with a Dewar seal of which the inner wall was maintained at 120° and the outer wall at −30°; tetraborane was added so that the pressure did not fall below its vapour pressure.[414–15] Other workers have reported a similar method.[416]

HEXABORANE(10)

Stock[32] has reported that very small quantities of B_6H_{10} were obtained by pyrolyzing diborane(6), tetraborane(10) or pentaborane(11). The pyrolysis of diborane at 225° has also been used to prepare hexaborane(10).[417–18]

DECABORANE(14)

Stock[32] was the first to report that $B_{10}H_{14}$ could be prepared by pyrolysis of either diborane or tetraborane, the crystals being collected in cool parts of the apparatus. Industrial interest led to preliminary examinations of the diborane pyrolysis reaction[419], and 60% yields were obtained by pyrolysis at 150–160° for 15–30 min.[420] Subsequently diborane was pyrolyzed to decaborane in reasonably good yields by a variety of methods, including hot-tube systems and the use of diluents and catalysts, high pressure methods and liquid media and solvents. A detailed summary of the methods is given in reference 24. The pyrolysis of diborane by heat transfer from a hot inert gas has been studied[421], and the effects of a variety of gaseous elements on diborane pyrolysis at 150–230° have been investigated.[422] It was found that yields of decaborane were increased when the pyrolysis was carried out at 150° in the presence of the Lewis base, dimethyl ether, and that the yield was increased by addition of pentaborane(9).[423–5] The use of diethyl ether has also been reported.[426] No satisfactory solid catalyst was found for the conversion.[411, 427–30] The pyrolysis of diborane at high pressure has been shown to yield decaborane under appropriate conditions.[389, 431–3]

Pyrolysis of tetraborane[434–5] and co-pyrolysis of diborane–tetraborane[436] or tetraborane–pentaborane mixtures[413, 435, 437–9] under pressure have been investigated. Hot-tube pyrolysis methods at atmospheric pressure have also been investigated[440], and multistage reactors have been developed.[441–2] Recycling systems have been developed which produced yields of 60% at 40 mm pressure pentaborane(9) and 500 mm pressure diborane at 148–165° for 30 s contact time[443–4], and a continuous-flow reactor system has been described.[445] Pre-pilot-plant scale studies have been made[446–7], typically with yields of 50–60% $B_{10}H_{14}$. Hot–cold reactor systems have been able to produce 30% decaborane(14).[448–9] Adiabatic compression methods of pyrolyzing diborane were found to have serious limitations.[385, 450]

Studies of pyrolysis in liquid media have used 2,3-dimethylbutane[451–2], and a variety of liquid solvents and catalysts.[453–5] Pilot-plant studies in hydrocarbon solvent have been made[456], and pre-pilot investigations used to determine optimum conditions[457–8], for a decaborane plant.[387] The pyrolysis of diborane in hexane under pressure has been studied[459], and a countercurrent process using cyclohexane has been developed.[416, 460–1] A quench consisting of the liquid fraction of pyrolysis products has been used in the vapour-phase pyrolysis of diborane.[462] Kerosene extraction and sublimation have been used to separate decaborane from polymeric solid hydrides.[463]

Co-pyrolysis of diborane and pentaborane(9) has yielded a number of products, four of which are unusual, viz. B_8H_{16}, $B_{10}H_{20}$ and two isomers, $B_{10}H_{18}$. The mass spectra of these boranes have been described.[463a]

Alkyl decaboranes have also been reported from the pyrolysis of diborane and alkylboranes in the presence of a nickel catalyst.[464]

HIGHER HYDRIDES

The new stable borane $B_{16}H_{20}$ was first obtained by pyrolysis of $B_9H_{13}SMe_2$.[465] Several workers have reported studies on the pyrolysis of decaborane(14).[466–8]

A general discussion of the production of reduced boron compounds and boron hydrides has appeared.[469]

Mechanisms of pyrolysis and interconversions among the boranes are discussed in subsection F after the other preparative techniques have been reviewed.

C. Protonation of Borane Anions

Diborane can be prepared by the simple method of treating a borohydride with a proton-donating species or Lewis acid:

$$BH_4^- + H^+ \rightarrow \tfrac{1}{2}B_2H_6 + H_2$$
$$BH_4^- + A \rightarrow \tfrac{1}{2}B_2H_6 + AH^-$$

The method can be extended to the preparation of some higher boranes from some larger borane anions.

The process may occur as a simple addition, converting the borane anion directly to the corresponding hydride, e.g.:

$$B_{10}H_{13}^{-} + H^{+} \rightarrow B_{10}H_{14}$$

or it may occur with evolution of hydrogen:

$$B_{10}H_{14}^{2-} + 2H^{+} \rightarrow B_{10}H_{14} + H_2$$

Alternatively, it can be a more complex process if the hydride species initially formed is unstable, and a variety of condensation or fragmentation products may be observed.

Slow addition of $Me_4N^{+}B_3H_8^{-}$ to polyphosphoric acid under vacuum yielded 43% tetraborane(10), 14% of the mixed pentaboranes, 4% of hexaborane(12), and traces of diborane and other hydrides[126], including octaborane(18) and nonaborane(15).[134-5, 470-1]

Pentaborane(9) and μDB_5H_8 have been obtained from $B_5H_8^{-}$ [106, 472], and B_6H_{10} has been regenerated from $B_6H_9^{-}$.[117]

When a tetramethylammonium salt of the '$B_8H_{12}^{-}$' ion (previously prepared from sodium hydride or sodium amalgam and B_8H_{12}) was treated with hydrogen chloride under carefully controlled conditions, the unstable hydride B_8H_{14} was isolated.[133]

Slow addition of $Et_3NH^{+}B_9H_{14}^{-}$ to polyphosphoric acid under vacuum yielded 40% diborane, 37% tetraborane(10), 10% mixed pentaboranes, 2·5% hexaborane(10) and traces of the higher hydrides B_8H_{12} and $B_{10}H_{14}$.[473] Under different conditions, treatment of KB_9H_{14} with dry HCl at −80° yielded iso-nonaborane(15)[143], which underwent decomposition above −35° to yield B_8H_{12}, $B_{10}H_{14}$ and n-$B_{18}H_{22}$.[474]

Treatment of sodium tridecahydrodecaborate(1−) with hydrogen chloride regenerates decaborane(14) in good yield, although the yields from alkylammonium salts are poor.[293, 475]

Acidification of aqueous $B_{10}H_{14}^{2-}$ solutions has been shown to produce the $B_{10}H_{15}^{-}$ ion[160]; the reaction was readily reversible. $B_{10}H_{14}^{2-}$ reacts with anhydrous hydrogen chloride to produce $B_{10}H_{14}$ and uncharacterized chlorination products.[476]

When an ethanolic solution of the triethylammonium salt of $B_{20}H_{18}^{2-}$ was passed through an acidic ion-exchange resin, n-$B_{18}H_{22}$ was produced as the major product in up to 60% yield[279, 477], and i-$B_{18}H_{22}$ was obtained as a minor byproduct of the reaction.[179, 180]

In summary the higher boranes which have been obtained by protonation of an anion, together with their precursors, are listed below:

Hydride	*Anions*
B_5H_9	$B_3H_8^{-}$, $B_5H_8^{-}$, $B_9H_{14}^{-}$
B_5H_{11}	$B_3H_8^{-}$, $B_9H_{14}^{-}$
B_6H_{10}	$B_6H_9^{-}$, $B_9H_{14}^{-}$
B_6H_{12}	$B_3H_8^{-}$
B_8H_{12}	$B_9H_{14}^{-}$
B_8H_{14}	'$B_8H_{12}^{-}$'
B_8H_{18}	$B_3H_8^{-}$
B_9H_{15}	$B_3H_8^{-}$
i-B_9H_{15}	$B_9H_{14}^{-}$
$B_{10}H_{14}$	$B_9H_{14}^{-}$, $B_{10}H_{13}^{-}$, $B_{10}H_{14}^{2-}$
n-$B_{18}H_{22}$	$B_9H_{14}^{-}$, $B_{20}H_{18}^{2-}$
i-$B_{18}H_{22}$	$B_{20}H_{18}^{2-}$

D. Electrical Discharge and Radiation Methods

A number of the less accessible boranes have been prepared by electrical discharge and irradiation methods. The effect of discharges has been studied on diborane, pentaborane and decaborane vapours either alone, or diluted with hydrogen, and on mixtures of, e.g., diborane and pentaborane. Similarly, the deuteron irradiation of a number of boron hydrides and mixtures has been studied.

Inorganic syntheses with electric discharges have been discussed by Jolly.[478]

ELECTRIC DISCHARGE IN DIBORANE

An early isolation of hexaborane(10) was reported from the products of an electric discharge in gaseous diborane.[112] Other workers have reported the isolation of 40% B_4H_{10}, 20% B_5H_9, 30% B_5H_{11} and small quantities of B_6H_{10} and B_9H_{15} from a 15,000-V silent discharge in diborane diluted with helium.[355] B_6H_{12} and several 'heptaboranes' were claimed to be observed mass-spectrometrically in addition to the lower hydrides and B_9H_{15} in the products of electric discharges in diborane.[347, 350]

When a 2:1 mixture of diborane(6) and pentaborane(9) was passed in hydrogen through a 2700-V a.c. electric discharge, octaborane(12) was isolated from among the hydrides produced.[129, 130]

ELECTRIC DISCHARGE IN PENTABORANE(9) AND DECABORANE(14)

When B_5H_9 and hydrogen were passed slowly through a glow discharge between copper electrodes, a solid was formed which was shown to be $B_{10}H_{16}$.[175, 296, 479]

When decaborane vapour was passed in a current of hydrogen through a 1700-V a.c. discharge between copper electrodes, the stable hydride $B_{20}H_{16}$ was produced.[87, 90, 480]

Reports have been made of attempts to prepare B_5H_9[383, 481] and B_5H_{11}[482–3] by discharge methods.

RADIATION METHODS

Hall and Koski have reported preparation of $B_{10}H_{16}$, $B_{11}H_{17}$, $B_{14}H_{22}$, $B_{15}H_{21}$ and $B_{20}H_{26}$ from the deuteron irradiation of respectively pentaborane(9), pentaborane(9) plus hexaborane(10), tetraborane(10) plus decaborane(14), pentaborane(9) plus decaborane(14), and decaborane(14).[189, 484]

Gamma-radiolysis of pentaborane(9) vapour has also been studied.[485] The photolysis of diborane at 1894 Å has been investigated and shown to lead to some B_5H_{11} and BH polymer.[486] The synthesis of higher boron hydrides by irradiation has been summarized.[487]

E. Chemical Methods of Preparation and Interconversion

There are a number of reactions which produce boron hydrides by an apparently haphazard variety of routes. One development of significance was the observation of cleavage of boron hydrides by Lewis bases. This is now becoming an important method for preparing hydrides, wherein a relatively unstable hydride is treated with a judiciously chosen Lewis base to bring about interconversion.

Methods which have been used to prepare individual hydrides are summarized below.

PENTABORANE(9)

Edwards and co-workers have reported that Lewis-base–triborane adducts catalyze the slow conversion of tetraborane(10) to pentaborane(9).[488]

$$5B_4H_{10} + LB_3H_7 \rightarrow 2B_5H_9 + 2B_2H_6 + L$$

Bis(dimethylamino)borane also catalyzed the formation of B_5H_9 from tetraborane(10) and from pentaborane(11).[489, 490, 490a]

Hexaborane(12) is quantitatively converted to pentaborane(9) and diborane in the presence of dimethyl ether.[126]

$$B_6H_{12} \xrightarrow{Me_2O} B_5H_9 + \tfrac{1}{2}B_2H_6$$

PENTABORANE(11)

Specifically base-boron-labelled pentaborane(11) has been prepared by treating isotopically normal tetraborane carbonyl B_4H_8CO with ^{10}B isotopically enriched diborane[491]:

$$B_4H_8CO + B_2H_6 \rightarrow B_5H_{11} + BH_3CO$$

HEXABORANE(10)

Hexaborane(10) has been prepared by treating pentaborane(11) with a variety of basic reagents.[489, 490, 490a, 492–5] Yields of up to 30% have been obtained, together with diborane, tetraborane, pentaborane(9), decaborane and polymeric hydrides, although a later report[261] suggested that the products also contained nonaborane(15). A recent report[496] suggests that the best synthesis of hexaborane(10) from pentaborane(11) occurs in over 40% yield.

It has been suggested[497] that the overall decomposition of pentaborane(11) in bases proceeds according to the equation:

$$2B_5H_{11} \xrightarrow{Me_2O} B_6H_{10} + 2B_2H_6$$

Hexaborane(10) was found as a minor product when tetraborane(10) was treated with sodium hydride in ether[498], and the postulated side reaction was[499]

$$2B_4H_{10} \xrightarrow{Et_2O} B_2H_6 + B_6H_{10} + 2H_2$$

Hexaborane(10) is also formed as one of the decomposition products of B_9H_{15}.[131, 500]

An incompletely characterized isomer of B_6H_{10} has been briefly reported from the reaction of diborane with the $B_5H_8^-$ ion, and this isomer is converted to normal B_6H_{10} on standing for 30 min at room temperature.[106]

$$MB_5H_8 + B_2H_6 \rightarrow MBH_4 + i\text{-}B_6H_{10}$$

HEXABORANE(12) AND OCTABORANE(12)

B_6H_{12} was prepared by decomposition of pentaborane(11) and purified by gas chromatography.[128, 501]

B_8H_{12} has been shown to be the immediate product of decomposition of B_9H_{15} [131, 500, 502–3], and $i\text{-}B_9H_{15}$.[132–3, 474]

NONABORANE(15)

B_9H_{15} has been prepared by several routes from pentaborane(11). Early experiments[489, 490] on the reactions of pentaborane(11) with bases yielded hexaborane(10) fractions contaminated with nonaborane(15). Burg and Kratzer[261, 504] were later able to obtain B_9H_{15} in high purity by allowing B_5H_{11} to interact with a surface of hexamethylenetetramine. The reaction presumably occurs via the abstraction of a BH_3 unit by the ligand, followed by rapid reaction of the remaining B_4H_8 fragment with a further molecule of B_5H_{11}:

$$B_5H_{11} + L \rightarrow B_4H_8 + LBH_3$$
$$B_4H_8 + B_5H_{11} \rightarrow n\text{-}B_9H_{15} + 2H_2$$

B_9H_{15} has also been synthesized by the high pressure reaction between diborane and pentaborane(11).[131, 503]

The preparation of isotopically labelled $n\text{-}B_9H_{15}$ was accomplished using the reaction between octaborane(12) and ^{10}B-labelled liquid diborane(6) at −30°.[505–6]

$$B_8H_{12} + \tfrac{1}{2}B_2H_6 \rightarrow B_9H_{15}$$

DECABORANE(14)

Isotopically labelled decaborane(14) has been prepared by several routes. A decaborane(14) containing two labelled boron atoms probably in the 6,9 positions was prepared by treating isotopically normal octaborane ($^nB_8H_{12}$) with $^{10}B_2H_6$, and the following reaction mechanism was proposed to account for the observed products of the reaction.[505–6]

$$\begin{tikzcd} & n\text{-}{}^{10}\mathrm{B}^{n}\mathrm{B}_8\mathrm{H}_{15} \\ {}^{n}\mathrm{B}_8\mathrm{H}_{12}+\tfrac{1}{2}{}^{10}\mathrm{B}_2\mathrm{H}_6 \arrow[ur] \arrow[dr] & \\ & i\text{-}{}^{10}\mathrm{B}^{n}\mathrm{B}_8\mathrm{H}_{15} \end{tikzcd}$$

$$i\text{-}{}^{10}B^{n}B_8H_{15} \rightarrow i\text{-}{}^{10}B^{n}B_8H_{13}+H_2$$
$$i\text{-}{}^{10}B^{n}B_8H_{13} \rightarrow n\text{-}{}^{10}B^{n}B_8H_{13}$$
$$i\text{-}{}^{10}B^{n}B_8H_{13}+\tfrac{1}{2}{}^{10}B_2H_6 \rightarrow {}^{10}B_2^{n}B_8H_{16}$$
$$n\text{-}{}^{10}B^{n}B_8H_{13}+\tfrac{1}{2}{}^{10}B_2H_6 \rightarrow {}^{10}B_2^{n}B_8H_{16}$$
$${}^{10}B_2^{n}B_8H_{16} \rightarrow {}^{10}B_2^{n}B_8H_{14}+H_2$$

Isotopically labelled decaborane(14) has also been prepared by planned syntheses, involving the treatment of either $B_9H_{12}^-$ or $B_9H_{14}^-$ with hydrogen chloride and ^{10}B-diborane.[507–8] The isotopic distribution in the product decaborane(14) has been accounted for in terms of partial conversion between the postulated intermediates i-B_9H_{13} and n-B_9H_{13}, resulting in labelling in the 6,9, and 5,7,8,10 positions. A similar product was obtained from the reaction between i-B_9H_{15} and labelled diborane.[507–8] Decaborane(14) has also been isolated from the products of heating the $B_5H_8^-$ ion with diborane in glyme solutions.[106]

HEXADECABORANE(20) AND OCTADECABORANE(22)

$B_{16}H_{20}$ was isolated as one of the products of pyrolysis of $B_9H_{13}SMe_2$.[509] One of the two known isomers of $B_{18}H_{22}$ with m.p. 179–180° was produced by thermal decomposition of $B_9H_{15}SMe_2$[509, 510], and n-$B_{18}H_{22}$ was prepared by heating B_9H_{13},OEt_2.[474]

ICOSABORANE(16)

$B_{20}H_{16}$ has been prepared by the catalytic pyrolysis of decaborane(14).[88–9] The catalyst used was $MeNHBMe_2$ at a temperature of 350° at < 1 mm pressure.

A critical review of methods of synthesis of the boranes has recently appeared.[511]

F. Mechanism of Pyrolyses and Interconversions

In order to gain a better understanding of the processes occurring in the rather complicated syntheses described above and to optimize conditions for the production of any one particular borane, detailed study of the mechanistics and kinetics involved is essential. Most of the kinetic studies so far made have concerned the pyrolysis of diborane, since this is the most readily accessible starting material for the production of the higher boranes.

Pyrolysis of diborane or the lower hydrides leads to the higher hydrides, and eventually to polymeric materials and hydrogen. Early investigations of the pyrolysis of diborane[258, 370] indicated the equilibrium:

$$2B_5H_{11}+2H_2 \rightleftharpoons 2B_4H_{10}+B_2H_6$$

This reaction was later investigated by two workers[512–13] and the mechanism below was proposed[514]:

$$B_2H_6 \rightleftharpoons 2BH_3$$
$$BH_3+B_2H_6 \rightleftharpoons B_3H_7+H_2$$
$$B_3H_7+B_2H_6 \rightleftharpoons B_5H_{11}+H_2$$
$$B_5H_{11}+H_2 \rightleftharpoons B_4H_{10}+BH_3$$
$$B_4H_{10}+H_2 \rightleftharpoons 2B_2H_6$$
$$B_4H_{10} \rightarrow \text{Polymer}+xH_2$$
$$B_5H_{11} \rightarrow \text{Polymer}+yH_2$$
$$B_5H_{11} \rightarrow B_5H_9+H_2$$
$$B_5H_9 \rightarrow \text{Polymer}+zH_2$$

The dependence of the distribution of the products on the initial partial pressure of diborane was noted, and pentaborane(11) was the major product in the early stages of the reaction. In later stages, however, pentaborane(9) became the major constituent; these observations were confirmed by other workers.[515–18]

The kinetics of the diborane pyrolysis have also been studied by infra-red spectroscopy[519] and the rates of diborane disappearance agreed with the earlier work.[513] The diborane was observed to decompose by a second-order rate law below 150°, but at about 150° the reaction followed a 3/2-order law, and at pressures below 5 mm it became first-order. The decomposition of pentaborane(11) to pentaborane(9) was therefore postulated to be at least partly heterogeneous. Other investigations of the diborane pyrolysis have been made[520–1], and Bragg *et al.* found the rate determining step to be of 3/2-order.[522]

Experimental studies of the various steps in the thermal conversion of diborane to pentaborane(11) have been described in some detail[523–6], and the observation that the rate of decomposition of B_2H_6 at 100° is five times as fast as that of B_2D_6 has been used[524] to postulate that the step:

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

is rate controlling in Schaeffer's preferred mechanism:

$$\begin{array}{rcl}
B_2H_6 & \rightleftharpoons & 2BH_3 \\
BH_3 + B_2H_6 & \rightleftharpoons & B_3H_9 \\
B_3H_9 & \rightleftharpoons & B_3H_7 + H_2 \\
B_3H_7 + B_2H_6 & \rightleftharpoons & B_4H_{10} + BH_3 \\
B_4H_{10} & \rightleftharpoons & B_4H_8 + H_2 \\
B_4H_8 + B_2H_6 & \rightleftharpoons & B_5H_{11} + BH_3
\end{array}$$

Two workers[527–8] have reported an extensive study of the pyrolysis mechanism of diborane, and a number of co-pyrolysis studies were performed in which B_4H_{10}, B_5H_9, B_5H_{11}, $B_{10}H_{14}$ and hydrogen were added and the effects of each on the pyrolysis of diborane determined. The resulting mechanism was then proposed after the data had been processed by means of an analogue computer. Consistent with this mechanism was the experimental observation of BH_3 and B_3H_9 in the pyrolysis products of B_2H_6.[529]

$$\begin{array}{rcll}
B_2H_6 & \rightleftharpoons & 2BH_3 & (1) \\
BH_3 + B_2H_6 & \rightleftharpoons & B_3H_9 & (2) \\
B_3H_9 & \rightleftharpoons & B_3H_7 + H_2 & (3) \\
B_3H_7 + B_2H_6 & \rightarrow & B_5H_{11} + H_2 & (4) \\
B_3H_7 + B_2H_6 & \rightarrow & B_4H_{10} + BH_3 & (5) \\
B_5H_{11} & \rightarrow & B_4H_8 + BH_3 & (6) \\
B_4H_8 + H_2 & \rightleftharpoons & B_4H_{10} & (7) \\
B_4H_8 + B_2H_6 & \rightarrow & B_5H_{11} + BH_3 & (8) \\
B_4H_{10} & \rightarrow & B_3H_7 + BH_3 & (9) \\
B_5H_{11} & \rightarrow & B_5H_9 + H_2 & (10) \\
B_5H_9 + B_3H_7 & \rightarrow & B_8H_{14} + H_2 & (11) \\
B_8H_{14} & \rightarrow & B_8H_{12} + H_2 & (12) \\
B_8H_{12} + B_2H_6 & \rightarrow & B_{10}H_{16} + H_2 & (13) \\
B_{10}H_{16} & \rightarrow & B_{10}H_{14} + H_2 & (14) \\
B_{10}H_{14} + BH_3 & \rightarrow & B_{11}H_{15} + H_2 & (15) \\
B_{11}H_{15} + B_2H_6 & \rightarrow & B_{12}H_{12} + BH_3 + 3H_2 & (16) \\
B_{12}H_{12} & \rightarrow & \text{Polymer} & (17)
\end{array}$$

Studies to date strongly indicate that the initial pyrolysis of diborane occurs by a 3/2-order reaction, and until recently it has been generally accepted that the initiating reaction is step (1). The rate-controlling step involves a three-boron atom species, and step (3) has been proposed as the most likely. It is questionable whether step (4) is of significance in the scheme. Step (5) seemed to be important, since tetraborane could be isolated from the pyrolysis of diborane in a hot–cold reactor. The kinetics of the pyrolysis of tetraborane (first-order with respect to tetraborane, independence of diborane concentration, and inhibition by hydrogen) suggest that step (7) is important, and further support came from an investigation of the kinetics of the reaction of tetraborane(10) with carbon monoxide to form B_4H_8CO, which yielded an activation energy comparable with that for the pyrolysis of tetraborane.[523, 530] However, the reversibility or occurrence of step (7) has been questioned since no exchange between D_2 and B_4H_{10} was observed at 45° in 130 min.[531] Several workers have claimed to demonstrate the importance of step (8)[258, 515, 532–3], and the irreversibility of step (9).[527, 534] Step (10) is probably irreversible since there is no evidence of lower boron hydrides from the pyrolysis of pentaborane(9).[535]

The application of isotopic substitution in elucidating the mechanisms has been discussed.[531, 536–8]

Very recently a complete reappraisal of the mechanism of thermal decomposition of diborane and of the interconversions of the boranes has been published[539] as a result of which it seems unlikely that the initiating stage is the dissociation of diborane into two BH_3 units (or into $BH_2 + BH_4$). Cogent evidence is adduced in favour of a bimolecular initiation between two molecules of diborane to give B_3H_9 and a BH_3 unit which reacts with a further molecule of diborane to produce a second B_3H_9 moiety. The rate-determining decomposition of B_3H_9 into B_3H_7 and hydrogen then establishes the overall 3/2-order of reaction as observed. The new unified scheme also interprets (a) the straight pyrolysis of B_4H_{10} and B_5H_{11}, (b) the effect of hydrogen on the decomposition of each borane, (c) the co-pyrolysis of B_2H_6 with B_4H_{10}, B_5H_{11} and B_5H_9, (d) the interconversion of the boranes, and (e) their behaviour in ^2D and ^{10}B isotope-exchange studies. The revised mechanism now proposed is as follows:

$$2B_2H_6 \rightleftharpoons BH_3 + B_3H_9 \tag{1}$$
$$BH_3 + B_2H_6 \rightleftharpoons B_3H_9 \tag{2}$$
$$B_3H_9 \rightleftharpoons B_3H_7 + H_2 \tag{3}$$
$$2B_3H_9 \rightarrow 3B_2H_6 \tag{3a}$$
$$BH_3 + B_3H_7 \rightleftharpoons B_4H_{10} \tag{4}$$
$$B_2H_6 + B_3H_7 \rightarrow BH_3 + B_4H_8 + H_2 \rightleftharpoons B_5H_{11} + H_2 \tag{5, 8}$$
$$B_3H_9 + B_3H_7 \rightarrow B_2H_6 + B_4H_{10} \tag{6}$$
$$2B_3H_7 \rightarrow B_2H_6 + B_4H_8 \tag{7}$$
$$B_3H_9 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11} + H_2 \tag{9}$$
$$B_3H_7 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11} \tag{10}$$
$$H_2 + B_4H_8 \rightarrow B_4H_{10} \tag{11}$$
$$BH_3 + B_4H_8 \rightleftharpoons B_5H_{11} \tag{12}$$
$$B_3H_9 + B_4H_8 \rightarrow B_2H_6 + B_5H_{11} \tag{13}$$

Apart from hydrogen, the only readily isolable products from the pyrolysis of B_2H_6 are B_4H_{10}, B_5H_{11}, B_5H_9, $B_{10}H_{14}$ and a non-volatile hydride of composition $(BH)_x$, though small quantities of B_6H_{10} are sometimes observed. All other species in the scheme are short-lived. The rate-controlling step is (3) which is slow compared with the disappearance of B_3H_9 to reform B_2H_6 by (3a). Because of the relative concentrations, reaction (3a) will be considerably more important than the reverse of reaction (1) and will thus be mainly responsible for fixing an upper limit on the floating concentration of B_3H_9; provided that this floating concentration is maintained it is immaterial to the overall kinetics how the B_3H_9 is formed, whether by reactions (1) and (2) or by some other path.

In support of this revised scheme it is shown that reaction (1) requires less energy than the simple dissociation $B_2H_6 \rightarrow 2BH_3$ and arguments are adduced which suggest that the reverse reaction $2BH_3 \rightarrow B_2H_6$ is also difficult because of the geometry and bonding of the two reacting species. Experimental evidence comes from the rates and products of pyrolysis reactions at very low pressures (10^{-5}–10^{-8} atm) and high temperatures 250–480°C.

Subsequent steps in the reaction have also been carefully documented[539] and it is concluded that B_4H_{10} appears as an isolable intermediate before B_5H_{11}. Neither

B_5H_9 nor higher boranes are formed in detectable amounts until after the appearance of B_5H_{11}. In spite of their vital role, hexaboranes usually escape observation when diborane is pyrolyzed because of their short lives relative to the much more stable B_5H_9 and $B_{10}H_{14}$. In fact, only recently has it been possible to prove that B_6H_{12} is formed from the lower boranes.[128] The evidence suggests that the most significant steps are[539]:

$$2B_3H_7 \rightarrow B_6H_{12}+H_2 \tag{7a}$$
$$B_3H_7+B_4H_8 \rightarrow B_2H_6+B_5H_9 \tag{14}$$
$$2B_4H_8 \rightarrow B_3H_7+B_5H_9 \rightarrow B_2H_6+B_6H_{10} \tag{15, 17}$$
$$2B_4H_8 \rightarrow B_2H_6+B_6H_{10} \tag{15a}$$
$$B_4H_8+B_5H_9 \rightarrow B_3H_7+B_6H_{10} \tag{18}$$
$$B_6H_{12} \rightarrow BH_3+B_5H_9 \tag{19}$$
$$B_3H_7+B_6H_{12} \rightarrow B_4H_8+B_5H_{11} \tag{20}$$
$$B_4H_8+B_6H_{12} \rightarrow B_5H_9+B_5H_{11} \tag{21}$$
$$B_4H_8+B_6H_{12} \rightarrow 2B_5H_9+H_2 \tag{23}$$

It is to be noted that B_5H_9 is formed in various transfer and elimination reactions (14, 15, 19, 21, 23) but not by direct elimination of hydrogen from B_5H_{11} which is both mechanistically unlikely and experimentally unsubstantiated, since when B_5H_{11} is pyrolyzed alone the main product is B_2H_6.

There are two principal routes from the lower boranes to $B_{10}H_{14}$[539]: one from B_5H_{11} avoiding B_5H_9 (which can be called the low-temperature route), and the other via B_5H_9 (the high-temperature route). The two most important reactions are probably:

$$B_4H_8+B_5H_{11} \rightarrow n\text{-}B_9H_{15}+2H_2 \tag{16}$$

and

$$B_3H_7+B_6H_{10} \rightarrow n\text{-}B_9H_{15}+H_2 \tag{22}$$

Thus when B_5H_{11} and B_2H_6 were held together under pressure at room temperature for a few days almost the only higher borane produced was n-B_9H_{15} in high yield[131]; the virtual absence of B_6, B_7, B_8 and B_{10} species implies a single jump of four boron atoms. The high-temperature route arises because, once the non-icosahedral species B_5H_9 is formed, the higher stability of this borane requires a higher temperature for its conversion. It is also relevant that pyrolysis of B_5H_9 alone gives a non-volatile solid as the main product whereas it readily co-pyrolyzes with diborane at a lower temperature to yield mainly $B_{10}H_{14}$; i.e. B_5H_9 is attacked by fragments produced by the thermally less stable B_2H_6 thus enabling its conversion by reactions (17) and (18) to B_6H_{10} which then reacts as in equation (22).

There is good evidence from isotope studies that n-B_9H_{15} does not lead to $B_{10}H_{14}$ in a single step, the most probable sequence of reactions being[539]:

$$n\text{-}B_9H_{15} \rightleftharpoons BH_3+B_8H_{12} \tag{25}$$
$$B_3H_7+B_8H_{12} \rightarrow B_2H_6+B_9H_{13} \tag{27}$$
$$B_3H_7+B_9H_{13} \rightarrow B_2H_6+B_{10}H_{14} \tag{28}$$

Other concurrent reactions are:

$$B_8H_{12} \rightarrow B_6H_{10}+B_2H_2\text{(polymerizes)} \tag{24}$$

and

$$B_3H_9+B_8H_{12} \rightarrow B_2H_6+n\text{-}B_9H_{15} \tag{26}$$

In summarizing the preceding reaction scheme it can be seen that the four main modes of reaction of borane species at moderate temperatures are: (a) exchange of BH groups, (b) exchange of BH_3 groups, (c) release of BH_3 molecules by unimolecular dissociation, and (d) condensation with release of hydrogen. It is notable that BH_2 groups are never exchanged; this is a consequence of the fact that, for all known boranes of formula B_pH_q, p and q are either both even or both odd, so that this condition must also obtain for the groups they exchange.

OTHER PYROLYSIS STUDIES

The kinetics of the pyrolysis of tetraborane(10) have been described[532–3], with the results already mentioned.

The gas-phase pyrolysis of pentaborane(9) yielded a first-order homogeneous reaction mechanism with an activation energy of $33{\cdot}9 \pm 1{\cdot}1$ kcal mole^{-1}.[535] Study of the liquid pyrolysis yielded a similar activation energy (34·2 kcal mole^{-1}) but the reaction was found to be of second order.[540] A flow system has also been used to study this reaction.[541]

The kinetics of the pyrolysis of decaborane(14) have been examined over the temperature range 170–238°; it was shown to be a homogeneous vapour-phase reaction, which was first-order with respect to decaborane, and which had an activation energy of 41·4 or $41{\cdot}6 \pm 0{\cdot}5$ kcal mole^{-1}.[468, 521, 542–4]

PART 6: CHEMICAL PROPERTIES OF THE BORON HYDRIDES

Certain chemical properties of the boron hydrides can be predicted to some extent from knowledge of their structures and from calculations of charge density within the molecules, although caution must be used in inferring detailed chemical behaviour from these methods. Difficulties arise in chemical predictions in a number of reactions in which the detailed mechanism cannot be known with certainty, and also where steric or kinetic effects may have a marked influence on the course of a reaction.

The effect of structure on chemical behaviour is most noticeable in the facile cleavage of BH_3 groups from molecules containing BH_2 units, particularly where these are bonded to the rest of the molecule by bridge-hydrogen atoms. The effect of charge density within the molecules has been best demonstrated for the two hydrides B_5H_9 and $B_{10}H_{14}$, whose chemical properties have been by far the most extensively investigated.

The fact that the compounds are ‘electron deficient’ in the specific sense of having fewer electrons available than orbitals available for bonding (Part 3), leads inevitably to much of the chemistry being associated with electron-accepting or Lewis acid behaviour. This may take the form of the formation of stable adducts or the formation of anionic species, or may often involve species of these types as reaction intermediates with subsequent further reaction or degradation.

At the present time any classification of the chemical reactions of the higher boranes is bound to be arbitrary to some extent and some overlaps among the various categories of reaction are inevitable. However, several broad types of reaction can be distinguished and it will be convenient to consider these under the following headings:

A. Substitution of terminal hydrogen atoms.
B. Addition reactions.
C. Cleavage reactions.
D. Reactions involving loss or ionization of bridge-hydrogen atoms.
E. Electron-addition reactions.
F. Oxidation.
G. Hydrolysis, alcoholysis and reactions with mercaptans.
H. Other chemical reactions.

Within each category there may be various sub-categories and within these the boranes are considered individually according to the number of boron atoms they contain.

A. Substitution of Terminal Hydrogen Atoms

(i) ELECTROPHILIC SUBSTITUTION

Pentaborane(9); Halogen Substitution

Direct halogenation of pentaborane(9) with bromine or iodine produces 1-bromopentaborane(9) or 1-iodopentaborane(9).[103, 320–1, 545–6]

$$B_5H_9 + X_2 \rightarrow 1\text{-}XB_5H_8 + HX \qquad (X = \text{Br,I})$$

Halogenations may also be carried out in the presence of Friedel–Crafts catalysts to yield initially 1-substituted derivatives. 1-Chloropentaborane(9) was prepared by treating pentaborane(9) with chlorine at 0° in the presence of boron trichloride and aluminium chloride, but the absence of aluminium chloride led to 2-chloropentaborane(9) in low yield.[547] Chlorination of 2-chloropentaborane(9) in the presence of aluminium chloride produced 1,2-dichloropentaborane(9) which isomerized in the presence of hexamethylenetetramine to a mixture of 2,3- and 2,4-disubstituted derivatives. Friedel–Crafts chlorination of the mixture produced 1,2,3-trichloropentaborane(9).[548–9] A patent has been presented for the preparation of bromopentaborane(9).[550]

Other halogen-exchange or isomerization reactions of the halopentaboranes include the catalytic conversion of 1-iodopentaborane(9) to 2-iodopentaborane(9)[545–6], the preparation of 2-chloropentaborane(9) from 1-bromopentaborane(9) by exchange involving aluminium chloride[551], conversion of 1-iodopentaborane(9) to 1-chloropentaborane(9) with mercuric chloride[545–6], and the preparation of 2-fluoropentaborane(9) from 2-iodopentaborane(9) and antimony trifluoride.[545–6] Bases also catalyze the isomerization of 1-BrB_5H_8 to 2-BrB_5H_8.[552]

The structures of B_5H_8I[300] and B_5H_8Br[320–1] have been established by n.m.r. studies, and the ^{11}B n.m.r. of B_5H_8Cl at 32·5 MHz has shown basal substitution.[553]

The iodine n.q.r. spectrum of B_5H_8I shows a transition $\frac{1}{2} \rightarrow \frac{3}{2}$ at 196·2 MHz.[554]

The fragmentation patterns of halogenated pentaboranes have also been described.[555]

Pentaborane(9); Friedel–Crafts Alkylation

The alkylation of pentaborane(9) by alkyl halides in the presence of Friedel–Crafts catalysts has been extensively reported. Methyl iodide and aluminium chloride produce 1-methylpentaborane(9).[556–8] A variety of other alkyl halides such as ethyl bromide, propyl chloride, *iso*-propyl chloride, *sec*-butyl chloride, and other Friedel–Crafts type catalysts such as ferric chloride and stannic chloride have also been used.[556, 558–67] In addition, the compounds $(B_5H_8)_2CH_2$ and $B_5H_8CH_2BCl_2$ have been reported from the reactions of CH_2Cl_2, CH_2Br_2, CH_2ClBr with pentaborane(9) in the presence of aluminium chloride[568–9], although some workers failed to isolate similar products.[570] Benzene and alkylbenzenes react with pentaborane(9) to give solid products.[571]

Friedel–Crafts type of alkylation of pentaborane(9) has also been carried out using ethers and alcohols[572–3], boron trifluoride etherates[574], orthosilicates[575], and alkylborates.[576–7]

The structure of ethylpentaborane(9) was established by n.m.r. spectroscopy[321] and spectra of more fully ethylated products have also been reported.[328] The thermal decomposition of ethylpentaborane in the gas phase has been described.[578] Pentaborane has also been suggested as a catalyst for the polymerization of olefins[579] and diolefins[580] and has been used in the production of organopolysiloxanes.[581]

Pentaborane(9); Proton–deuterium exchange

Pentaborane(9) has been shown to undergo Friedel–Crafts proton–deuterium exchange at the 1-position with DCl catalyzed by aluminium chloride.[582–3] With silane-d_4, no exchange was observed at room temperature, but deuterium substitution occurred at three positions at 125°C, and addition of aluminium chloride catalyst resulted in deuteration at five positions.[584]

Pentaborane(9); 1-H or 1-alkyl rearrangements

Intramolecular deuterium–hydrogen exchange occurs in 1-deuteriopentaborane(9) when catalyzed by 2,6-dimethylpyridine at room temperature. At elevated temperatures (145°) an intermolecular exchange process takes place.[585] Similarly, 1-methyl- and 1-ethyl-pentaborane(9) rearrange under the influence of 2,6-dimethylpyridine to the 2-substituted derivatives[586], and thermal rearrangement also occurs.[587] The mechanisms of alkyl pentaborane(9) isomerizations have been discussed.[588–91]

An alkyl-substituted $B_5H_8^-$ ion has been isolated as an intermediate in the isomerization of 1-ethylpentaborane(9) with trimethylamine, and was identified as $Me_3NH^+B_5H_7C_2H_5^-$.[589, 592]

The fact that Friedel–Crafts halogenation, hydrogen exchange, or alkylation, i.e. electrophilic attack, occurs at the apex boron has been rationalized on the basis of the high electron-density present on the 1-boron atom in the ground-state pentaborane(9) molecule.

A variety of substituted pentaboranes have been made from reactions of LiB_5H_8 with element-halogen species (see Part 9). In addition, 2-ClB_5H_8 has been found to react with $NaMn(CO)_5$ and $NaRe(CO)_5$ to yield 2-$(CO)_5MnB_5H_8$ and 2-$(CO)_5ReB_5H_8$[593], and 1-IB_5H_8 gave 2-$MeOB_5H_8$ on treatment with Me_2O.[594–5] The microwave spectrum, vibration–rotation interaction, molecular structure and dipole moment of 1-MeB_5H_8 have recently been described.[596]

Pentaborane(11)

In contrast to pentaborane(9), the reaction between pentaborane(11) and alkyl halide in the presence of aluminium chloride did not yield an alkyl pentaborane(11), but produced instead the alkane and halopentaborane(11).[597]

Hexaboranes, Octaboranes and Nonaboranes

No electrophilic substitution reactions have been reported for these compounds.

Decaborane(14); Halogenation

The halogenation of $B_{10}H_{14}$ was first studied by Stock[32] who found that halogens reacted very slowly with decaborane to form disubstituted derivatives as the most stable products. The direct iodination of decaborane was shown to lead to two monoiododecaboranes and two diiododecaboranes.[598] The substitution isomers of the monoiododecaboranes were initially suggested to be 2-iododecaborane and 5-iododecaborane, although the second isomer was subsequently thought rather to be 1-iododecaborane[314, 322], and later studies confirmed this.[156, 599] The iodination in carbon disulphide solution in the presence of aluminium chloride was also shown to lead to 1-iododecaborane and 2-iododecaborane in a similar ratio to that observed in the direct reaction.[599, 600] Iodination with $ICl/AlCl_3$ also yields similar products.[599, 601] One of the diiododecaboranes was originally identified as 2,4-diiododecaborane[157, 598], and the second isomer is now accepted to be the 1,2-isomer.[599] The reaction of bromine in the presence of aluminium chloride with decaborane leads to monobromodecaborane(14)[602], which may also be prepared by treating decaborane with ethylene bromide in the presence of ferric chloride.[603]

The reaction of haloforms with decaborane in the presence of Friedel–Crafts catalysts has been reported to yield mono- and di-halogenated derivatives.[604] A similar method has been used to prepare 1- and 2-chlorodecaboranes by treating decaborane with 1,1-difluoroethane and aluminium chloride.[605]

In the presence of methanol, decaborane reacts with iodine according to the equation[606]:

$$B_{10}H_{14} + 20I_2 + 30MeOH \rightarrow 10B(OMe)_3 + 40HI + 2H_2$$

The structure of $B_{10}H_{13}I$ was investigated by n.m.r. spectroscopy[320, 322–3] and two isomers of $B_{10}H_{13}Cl$ were identified by this technique as 1-$ClB_{10}H_{13}$ and 2-$ClB_{10}H_{13}$.[324]

The iodine n.q.r. spectrum of $B_{10}H_{13}I$ showed a $\frac{1}{2} \rightarrow \frac{3}{2}$ transition at 190·8 MHz.[554]

Detailed study of the polarized u.v. spectrum of 2,4-$I_2B_{10}H_{12}$ is also reported.[211]

Decaborane(14); Friedel–Crafts Alkylation

The Friedel–Crafts alkylation of decaborane using alkyl halides and catalysts such as aluminium chloride, ferric chloride, etc., has been studied in some detail.

A number of industrial investigations into the Friedel–Crafts alkylation of decaborane have been carried out in search for high-energy boron fuels. Thus dimethyldecaborane[561] and polyalkylated decaboranes[607] were obtained from Friedel–Crafts alkylations with alkyl halides. A number of patents for the methylation and ethylation of decaborane using alkyl halides and aluminium chloride or boron trichloride with or without solvent have appeared.[608–12] Triethyl- and monopropyl derivatives have been described.[613] In addition, patents have appeared describing Friedel–Crafts alkylation using ferric chloride[614], the preparation of $B_{10}H_{13}CH_2Cl$ from $B_{10}H_{14}$, aluminium bromide and CH_2Cl_2[615], and the formation of

$$B_{10}H_{13}(CH_2)_2B_{10}H_{12}(CH_2)_2B_{10}H_{12}(CH_2)_2Cl$$

using ethylene dichloride and aluminium chloride or bromide.[616] Detailed study of catalysts in the methylation of decaborane has been made[617], and the methylation has been examined on a pre-pilot scale to evaluate the decaborane conversion, the alkylate composition and other details.[618]

The products of the Friedel–Crafts methylation of decaborane have been examined by gas chromatography and n.m.r. spectroscopy. The compounds identified were 2-methyl-, 2,4- and 1,2-dimethyl-, 1,2,3- and 1,2,4-trimethyl- and 1,2,3,4-tetramethyldecaborane(14).[619] The products obtained are entirely consistent with electrophilic attack at borons of highest electron density, and the experimental data are consistent with the calculated electron densities at positions 2,4 and 1,3. This observation is supported by n.m.r. study of some ethylated decaboranes.[328]

The kinetics of the gas-phase reaction of decaborane with ethyl bromide[620], and the condensed-phase Friedel–Crafts ethylation using ethyl chloride and aluminium chloride in cyclohexane[621] have been studied.

Other industrial work has been discussed in the reports.[449, 456, 622–6] The thermal decomposition of 2-ethyldecaborane has also been described.[627]

Decaborane(14); Friedel–Crafts Proton–Deuterium Exchange

Dupont and Hawthorne have reported that deuterium chloride exchanges with the protons in the 1,2,3,4-positions in the presence of aluminium chloride in carbon disulphide.[628–9]

n- and i-Octadecaborane(22)

Direct iodination of n-$B_{18}H_{22}$ yields n-$B_{18}H_{21}I$[297], although the position of substitution has not been determined.

Friedel–Crafts deuterium exchange in n- and i-$B_{18}H_{22}$ results in six deuterium atoms per molecule[297], terminally substituted in three pairs. The positions of substitution are most probably the 4,4′-, 2,2′- and 3,3′-sites, which have been calculated to be the sites of greatest electron density.[22]

Summary

The results of electrophilic substitution in the boron hydrides are consistent with calculations of ground-state electron densities in the molecules.[630] Thus in pentaborane(9), the apex position 1 carries $-0{\cdot}36e$ excess charge and the base borons 2,3,4,5 carry $+0{\cdot}25e$ charge.[22] More recent calculations[205a] modify the numerical values of these changes but not the fact that the apex boron has the greater electron density. It is the apex boron which is susceptible to electrophilic attack. In decaborane(14), the 2,4 positions carry[22] $-0{\cdot}10e$ charge, the 1,3 positions $-0{\cdot}04e$, the 5,7,8,10 positions $+0{\cdot}12e$ and the 6,9 positions $+0{\cdot}33e$. These values are however sensitive to the method of calculation. Electrophilic substitution occurs at the 1,2,3,4 positions exclusively, and with a slight preference for the 2,4 positions. In n-$B_{18}H_{22}$, positions 4,4′ carry $-0{\cdot}47e$, positions 2,2′ $-0{\cdot}35e$, the 3,3′ positions $-0{\cdot}06e$ and the 1,1′ positions $-0{\cdot}05e$.[22] Electrophilic substitution positions appear to occur at the 4,4′, 2,2′ and 3,3′ sites.

Despite this pleasing agreement between theoretical calculations and experimental observations care should be exercised in predicting chemistry from ground-state charge distributions. In order for such predictions to be reliable, the transition state must resemble very closely the unperturbed molecule; moreover, although the calculated results and observed chemistry are in rough agreement, the detailed mechanistic path of electrophilic substitution has yet to be established with certainty.

(ii) NUCLEOPHILIC SUBSTITUTION

Nucleophilic substitutions are less well characterized in the boron hydrides than are the electrophilic substitutions already mentioned; nucleophilic attack by a variety of basic reagents is described below.

Pentaborane(9)

A possible example of nucleophilic substitution has been reported in the preparation of $Et_2B_5H_7$ from $Et_2B_2H_4$ and B_5H_9[631], although this must be regarded with some scepticism.[632]

Decaborane(14)

The reaction of methyl- or ethyl-lithium with decaborane leads to nucleophilic substitution[633]; the principal product is 6-methyl- or 6-ethyl-decaborane. On methylation, small amounts of 5-methyl-, 6,5(or 8)-dimethyl- and 6,9-dimethyl-decaboranes are formed. The reactions of decaborane with a number of organometallic reagents have been studied.[634] Cohen and Pearl[635] studied the alkylation of decaborane with organometallic reagents, and found that the addition of an alkyl halide[636], dialkyl sulphate or BF_3,Et_2O[637] improved the yield. Attempts to alkylate with diethylzinc failed, but produced instead the reaction:

$$Zn(C_2H_5)_2 + B_{10}H_{14} \rightarrow C_2H_6 + C_2H_5ZnB_{10}H_{13}$$

A similar reaction was observed with Grignard reagents and the decaborane Grignard reagents $B_{10}H_{13}MgI + B_{10}H_{12}(MgI)_2$ were formed.[638] A minor reaction of decaborane with MeMgI produced 6-methyldecaborane.[639] Alkyl decaboranes could be prepared from decaborane Grignard reagents by reactions using alkyl fluoride[640], and benzyldecaborane was obtained using benzyl chloride.[638] Allyl decaborane has been similarly prepared.[636, 641]

Nucleophilic Deuterium Exchange

Deuterium exchange with D_2O–dioxan mixtures occurred first with the bridge-hydrogen atoms[642], and similar results were obtained with DCl/dioxan solutions.[643] It was shown that under ionizing conditions the deuterium atoms slowly equilibrate with the neighbouring terminal hydrogen atoms at positions 5,6,7,8,9 and 10.[293, 643–4] It was thus possible to prepare decadeuterodecaborane(14) with deuterium atoms at all positions except 1,2,3 and 4.[629]

Nucleophilic Substitution in n- and i-$B_{18}H_{22}$[297]

When *n*-$B_{18}H_{22}$ was treated with Bu^nLi no alkylated product was isolated, but butane was evolved and the $B_{18}H_{20}^{2-}$ ion produced:

$$2Bu^nLi + B_{18}H_{22} \rightarrow 2Bu^nH + B_{18}H_{20}^{2-} + 2Li^+$$

n- or *i*-$B_{18}H_{22}$ underwent deuterium hydrogen exchange with D_2O or DCl–dioxan to replace four bridge hydrogens and two terminal hydrogen atoms, suggested to be at positions 9,9′.

(iii) BRIDGE HYDROGEN SUBSTITUTION

The substitution of deuterium for bridge-hydrogen atoms has been reported for decaborane(14)[293, 642–4], and *n*- and *i*-$B_{18}H_{22}$.[297] The reaction product[645] of ethylamine with $B_9H_{13}NH_2C_2H_5$ has been shown[136–8] to contain an ethylamine group in a position which would be occupied by a bridge-hydrogen atom in the hypothetical $B_8H_{13}^-$ ion. (See Part 2, structure 38).

Bridge-substituted pentaborane(9) compounds have been prepared by treating LiB_5H_8 with Me_3SiCl[646] or R_2PCl derivatives.[647–8] R_3GeX and R_3SnX were also suggested to react in a similar manner[646, 649, 650], and Me_2BCl gave μ-$Me_2BB_5H_8$ in good yield.[651]

B. Addition Reactions

(i) TERMINAL ADDITION

Pentaborane(9)

B_5H_9 can be alkylated directly with olefins at elevated temperatures[563, 652], and the reaction has been shown to be nucleophilic in character yielding base-substituted products.[653] *n*-Butyl-, sec-butyl-, isobutyl- and ethyl-pentaborane were prepared.[654–5] Pentaborane has also been reported to react with 1,3-butadiene to produce $(B_5H_8)_2C_4H_8$.[656–7] Nucleophilic addition of olefins also occurs with catalysis by bases such as amines[658–9], tetrahydrofuran[660], and alumina.[661] Electrophilic addition can be carried out using olefins and Friedel–Crafts catalysts to yield apex-substituted pentaboranes.[321, 557, 569, 607, 662–3] The reaction rate is increased by addition of hydrogen chloride[664], and activated alumina and various Lewis acids have also been investigated as catalysts.[665] The purification of alkylpentaboranes by heating over a ferric oxide catalyst has been reported.[666]

Pentaborane(11)

B_5H_{11} reacts[667] with ethylene to form ethylpentaborane(11) as a major product, although the position of addition was not unequivocally determined. Dimethylenetetraborane(8) was produced as a side product at 25°. Olefinic and acetylenic hydrocarbons react readily with pentaborane(11) to produce liquid or gel-like products.[668–9] Conjugated dienes, e.g. 1,3-butadiene or 1,3-cyclopentadiene, yield adducts.[670] Trivinylmethylsilane has also been reported to add to three molecules of B_5H_{11}.[671]

Decaborane(14)

$B_{10}H_{14}$ reacts with ethylene at 232° to produce ethylated decaboranes[672], but it was reported that the reaction proceeded at 100° in the presence of aluminium chloride[563], or at 195–200° at high (1000–1100 psig) pressure.[673] A number of reports of ethylation of decaborane with ethylene and aluminium chloride have appeared.[626, 674–6] The Friedel–Crafts addition of ethylvinylether to decaborane(14) using zinc chloride catalyst has been used to prepare β-ethoxyethyldecaborane.[677]

(ii) SKELETAL HOMONUCLEAR ADDITION

Skeletal homonuclear additions are principally involved in the synthesis of higher boranes from lower boranes particularly in the pyrolysis method. This has been discussed in detail in Part 5.

Octaborane(12) and iso-nonaborane(15)

As mentioned in Part 5, B_8H_{12} reacts with BH_3 to form *n*-B_9H_{15}.[505–6] Similarly, *iso*-nonaborane(15), generated from $B_9H_{14}^-$, reacts with diborane to form decaborane(14).[507–8]

$$B_9H_{14}^- + H^+ + \tfrac{1}{2}B_2H_6 \rightarrow B_{10}H_{14} + 2H_2$$

Decaborane(14)

$B_{10}H_{14}$ adds BH_4^- with elimination of hydrogen to form initially the $B_{11}H_{14}^-$ ion[169], but it has been suggested that this reaction proceeds via the $B_{10}H_{13}^-$ ion:

$$B_{10}H_{14} + BH_4^- \xrightarrow{R_2O} B_{10}H_{13}^- + R_2OBH_3 + H_2$$
$$B_{10}H_{13}^- + R_2OBH_3 \xrightarrow[R_2O]{90^\circ} B_{11}H_{14}^- + H_2 + R_2O$$

Further reaction with BH_4^- yields $B_{12}H_{12}^{2-}$.[678–9, 680] Similarly, decaborane(14) reacts with amine-boranes to form the $B_{12}H_{12}^{2-}$ ion[678–9, 681]:

$$B_{10}H_{14} + 2Et_3NBH_3 \rightarrow (Et_3NH)_2B_{12}H_{12} + 3H_2$$

In these syntheses it is also possible to use B_5H_9 or $B_{18}H_{22}$.[678]

(iii) SKELETAL HETERONUCLEAR ADDITION

Pentaborane(9)

B_5H_9 undergoes skeletal addition with carbon vapour produced in a carbon arc to form B_5CH_7 and two other products, one of which is believed to be $B_5C_2H_7$.[682] When pentaborane is heated with acetylene at 215°, amongst the products of the reaction are three isomers of C-methyl derivatives of CB_5H_9.[119] The reaction of pentaborane and acetylene in an electric discharge yields $B_3C_2H_5$[683–4], the two isomers of $B_4C_2H_6$[40], and $B_5C_2H_7$; the last compound has been reported from the reaction between B_5H_9 and acetylene under pressure at 250°.[685] Pentaborane(9) and alkynes react in the presence of bases such as 2,6-dimethylpyridine to produce dihydrocarborane derivatives of the type $B_4C_nH_{2n+4}$.[686–7] It was found that increasing the number of alkyl groups about the triple bond of the alkyne enhanced the reactivity towards pentaborane and resulted in increased yields of the corresponding 2,3-dicarbahexaborane(8).[688] When 1-methylpentaborane(9) was subjected to silent electric discharge, monocarbahexaborane(7), B_5CH_7, was isolated.[41]

Hexaborane(10) and Decaborane(14)

When dimethylacetylene was heated at 200° with B_6H_{10} in the gas phase, trace amounts of $Me_2C_2B_6H_6$ were obtained, but yields could be increased up to 12% by u.v. irradiation.[52]

When $B_{10}H_{14}$ is treated with alkynes in the presence of a base such as MeCN or Me_2S, derivatives of 1,2-dicarba*closo*dodecaborane(12) (carborane) are obtained.[689–94]

A number of other reactions have been reported which may be regarded as skeletal additions. Me_3NAlH_3 and decaborane yield $(Me_3NH)^+(B_{10}H_{12}AlH_2)^-$. Me_3NGaH_3 and decaborane yield $(Me_3NH)^+(B_{10}GaH_{16})^-$.[67, 695] Diethylcadmium reacts with $B_{10}H_{14}$ to form $CdB_{10}H_{12}$,2Solvent, and this compound ionizes to produce $[(B_{10}H_{12})_2Cd]^{2-}$.[58] Diorganozinc and magnesium compounds react similarly with decaborane(14).[696–7] The structures of these metal-containing compounds have been inferred from spectroscopic studies, and recent single-crystal *X*-ray studies[65a] on $[CdB_{10}H_{12}(Et_2O)_2]_2$ lead to the unique structure shown in Fig. 6.1. The structure of $[Zn(B_{10}H_{12})_2]^{2-}$ has already been mentioned on p. 258.

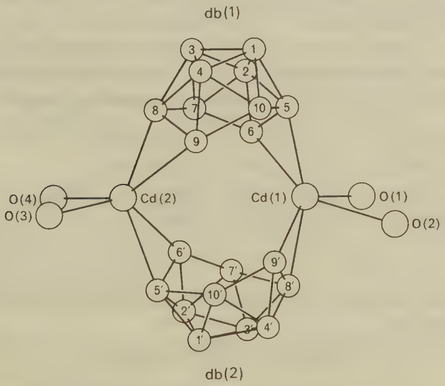
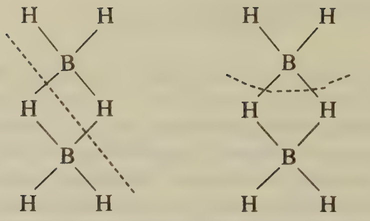


FIG. 6.1

C. Cleavage Reactions

Cleavage reactions of the boron hydrides have been discussed by Parry[697a, 698] in terms of symmetric and unsymmetric cleavage, in general brought about by nucleophilic reagents, by analogy with the reactions in diborane:

$$B_2H_6 + 2L \rightarrow 2L,BH_3$$
$$B_2H_6 + 2L \rightarrow L_2BH_2^+ BH_4^-$$



Symmetric cleavage Unsymmetric cleavage

The extensions to the higher hydrides were really applicable only to boranes in which there was a BH_2 group bonded to the remainder of the molecule by two hydrogen bridges. Symmetric cleavage was then described as cleavage which yields a neutral BH_3 species and a neutral higher borane fragment, each of which is coordinated with a molecule of the ligand. Unsymmetric cleavage was cleavage which yields the positively-charged BH_2-containing species $L_2BH_2^+$ and the negatively charged higher borane fragment. This classification suffers the disadvantage that a number of cleavage reactions of the boron hydrides fall into neither class, simply because the parent species contains no BH_2 groups. Cleavage of boranes by bases has been reviewed.[699, 701]

Pentaborane(9)

B_5H_9 has been observed to react with amines with cleavage. B_5H_9 readily absorbs 2 moles of Me_3N to give a solid adduct, which, in contact with excess of amine, slowly cleaves as follows[702–4]:

$$B_5H_9 + 2Me_3N \rightarrow B_5H_9(NMe_3)_2$$
$$B_5H_9(NMe_3)_2 + NMe_3 \rightarrow 2Me_3NBH_3 + (1/x)[B_3H_3(NMe_3)]_x$$

Without excess amine[488, 705] the compound slowly cleaved by the reaction:

$$B_5H_9(NMe_3)_2 \rightarrow Me_3NBH_3 + Me_3NB_4H_6$$

The reaction with dimethylamine, dimethylaminoborane or bis(dimethylamino)-borane produces the compounds[702] $(Me_2N)_3B_3H_3$ and $(Me_2N)_2B_4H_6$; the former compound has been shown to be trimeric dimethylaminoborane.[706] Similar reactions have been observed with Me_2NPMe_2.[707] The reactions of B_5H_9 with secondary amines have been reported.[703–4, 708] Reactions observed were

$$5B_5H_9(NHR_2)_2 \rightarrow 7B_2H_5NR_2 + 2BH_2NR_2 + 2H_2 + \text{Polymer}$$
$$B_5H_9(NHR_2)_3 \rightarrow 2B_2H_5NR_2 + BH_2NR_2$$
$$B_5H_9(NHR_2)_4 \rightarrow B_2H_5NR_2 + 3BH_2NR_2 + H_2$$
$$B_5H_9(NHR_2)_5 \rightarrow 5BH_2NR_2 + 2H_2$$

Pentaborane(11)

B_5H_{11} is cleaved by a number of reagents, the initial step being the 'symmetric' cleavage of a BH_3 group:

$$B_5H_{11} \rightarrow BH_3 + B_4H_8$$

Thus, carbon monoxide reacts with B_5H_{11} to form BH_3CO and B_4H_8CO[255, 709, 710], and PF_3 similarly forms BH_3PF_3 and $B_4H_8PF_3$.[255, 710] The reaction of pentaborane(11) with ethylene[667], and the exchange reaction between ethyldiborane and pentaborane(11)[632] also proceed by cleavage mechanism:

$$B_5H_{11} \rightleftharpoons BH_3 + B_4H_8$$
$$B_4H_8 + C_2H_4 \rightarrow C_2H_4B_4H_8$$
$$C_2H_4 + BH_3 \rightarrow C_2H_5BH_2$$
$$C_2H_5BH_2 + B_4H_8 \rightarrow C_2H_5B_5H_{10}$$
$$C_2H_5BH_2 + BH_3 \rightarrow C_2H_5B_2H_5$$
$$2C_2H_5BH_2 \rightarrow C_2H_5B_2H_4C_2H_5$$

A similar reaction was observed with 1,2-dimethyldiborane and pentaborane(11).[711]

The reactions of Lewis bases with pentaborane(11) are often complex[497], e.g. with trimethylamine the following reactions were suggested:

$$B_5H_{11} + 2Me_3N \rightarrow 2Me_3NBH_3 + B_3H_5$$
$$B_3H_5 \rightarrow \text{liquid hydrides} + \text{solid polymers} + H_2$$

The action of bases on pentaborane(11) has been used as a means of preparing a variety of otherwise difficultly accessible boron hydrides.[261, 489, 490, 494, 495, 712]

HEXABORANE(12)

B_6H_{12} reacts almost quantitatively with water to form tetraborane(10), and with dimethyl ether to form pentaborane(9).[126]

OCTABORANE(12) AND OCTABORANE(18)

B_8H_{12} reacts with water in diethyl ether solution to produce hexaborane(10) nearly quantitatively.[132–3] Treatment of B_8H_{18} with carbon monoxide at room temperature yielded BH_3CO, B_4H_{10} and B_4H_8CO.[135]

n- AND *i*-NONABORANE(15)

Both nonaboranes decompose readily with the initial formation of B_8H_{12}.[131–3, 474, 500, 502–3]

$$B_9H_{15} \rightarrow B_8H_{12} + BH_3$$

DECABORANE(14)

$B_{10}H_{14}$ can be degraded in aqueous alkali to the $B_9H_{14}^-$ ion[713]; the suggested mechanism is:

$$B_{10}H_{14} + OH^- \rightarrow B_{10}H_{13}^- + H_2O$$
$$B_{10}H_{13}^- + OH^- \rightarrow B_{10}H_{13}OH^{2-}$$
$$B_{10}H_{13}OH^{2-} + H_3O^+ + H_2O \rightarrow B_9H_{14}^- + B(OH)_3 + H_2$$

It is also cleaved by organic azides yielding tetrazaborolines and uncharacterized higher borane fragments[714–15]:

$$B_{10}H_{14} + 3RN_3 \rightarrow R_2N_4BH + H_2 + 2N_2 + [R,N,B_9,H_{11}]$$

Decaborane(14) is also solvolyzed in the presence of non-ionic ligands to form derivatives of the type $B_9H_{13}L$[716], and a similar reaction has been observed with the thiocyanate ion in aqueous dioxan to yield $B_9H_{13}NCS^-$.[717] Decaborane is more completely degraded by methanol to yield the $B_3H_8^-$ ion.[718a]

DECABORANE(16)

The central apex–apex B–B bond of $B_{10}H_{16}$ is slowly cleaved at room temperature by hydrogen iodide to yield B_5H_9 and B_5H_8I. At 100° the yield of B_5H_9 is quantitative, but the B_5H_8I reacts further. Similar reactions occur with hydrogen bromide at somewhat higher temperatures.[296]

D. Reactions Involving Loss or Ionization of Bridge–Hydrogen Atoms

PENTABORANE(9)

Early reports of the reaction of B_5H_9 with sodium hydride gave negative results.[716a, 717a] However, recent workers have found that alkali metal hydrides react with pentaborane(9) to liberate hydrogen and produce the $B_5H_8^-$ ion[591, 718]:

$$MH + B_5H_9 \rightarrow H_2 + MB_5H_8 \qquad (M = \text{Li, Na or K})$$

The reaction of pentaborane(9) with *n*-butyllithium was shown to proceed in a manner analogous with the minor reactions of decaborane(14), namely to produce the $B_5H_8^-$ ion[472]:

$$B_5H_9 + Bu^nLi \xrightarrow[-78^\circ \text{ to } -30^\circ]{Et_2O} LiB_5H_8 + BuH$$

Pentaborane(9) was regenerated from the lithium salt on treatment with hydrogen chloride, and the corresponding reaction with deuterium chloride led to bridge-deuterated pentaborane(9)[472]:

$$LiB_5H_8 + DCl \rightarrow \mu\text{-}DB_5H_8$$

Shore et al. were able to prepare $B_5H_8^-$ salts by the similar reactions of methyllithium, sodium hydride, or potassium hydride or other strong bases with pentaborane(9), and in addition isolated the stable Me_4N^+ salt.[106, 718–19]

HEXABORANE(10)

B_6H_{10} behaves similarly with methyllithium, sodium hydride, or potassium hydride to give $B_6H_9^-$.[117, 720]

OCTABORANE(12)

B_8H_{12} reacts with sodium hydride to evolve hydrogen and yield a product whose analysis was not certain, but suggested the formation of an ion of empirical formula $B_8H_{12}^-$. Treatment of this ion with hydrogen chloride produced the hydride B_8H_{14}[132–3]; the original species may have been dimeric or a mixture of $B_8H_{11}^-$ and $B_8H_{13}^-$.

DECABORANE(14)

Strong bases abstract a proton from decaborane under suitable conditions. Thus, the reactions of decaborane with a variety of basic anions lead to the (sometimes solvated) tridecahydrodecaborate(1 −) ion:

	Reference
$B_{10}H_{14} + H^- \xrightarrow[25°]{Et_2O} B_{10}H_{13}^- + H_2$	721–6
$B_{10}H_{14} + OH^- \longrightarrow B_{10}H_{13}^- + H_2O$	722, 727
$B_{10}H_{14} + OCH_3^- \longrightarrow B_{10}H_{13}^- + CH_3OH$	722, 725, 727
$B_{10}H_{14} + BH(OCH_3)_3^- \longrightarrow B_{10}H_{13}^- + B(OCH_3)_3 + H_2$	727
$B_{10}H_{14} + NH_2^- \longrightarrow B_{10}H_{13}^- + NH_3$	725
$B_{10}H_{14} + BH_4^- \longrightarrow B_{10}H_{13}^- + \frac{1}{2}B_2H_6 + H_2$	722, 725, 727

The last reaction has been shown to proceed in two stages involving the formation of the $B_{10}H_{15}^-$ ion and its subsequent decomposition[728]:

$$B_{10}H_{14} + BH_4^- \rightarrow B_{10}H_{15}^- + \tfrac{1}{2}B_2H_6$$
$$B_{10}H_{15}^- \rightarrow B_{10}H_{13}^- + H_2$$

The strong-acid behaviour of $B_{10}H_{14}$ has been known for some time[729] by titration in aqueous ethanol; similar titrations with aqueous alkali have shown the monoprotic behaviour of decaborane in aqueous acetone[730], acetonitrile[731–2], dimethylformamide[732] and in 96% diglyme plus 4% acetonitrile.[716] Similarly, decaborane behaved as a monoprotic acid when treated with diethylamine[475], triphenylphosphine methylene[733] or trimethylamine methylene[475]:

$$Ph_3\overset{+}{P}\text{—}\overset{-}{C}H_2 + B_{10}H_{14} \rightarrow Ph_3\overset{+}{P}CH_3B_{10}H_{13}^-$$
$$Me_3\overset{+}{N}\text{—}\overset{-}{C}H_2 + B_{10}H_{14} \rightarrow Me_4\overset{+}{N}B_{10}H_{13}^-$$

The 1,2,3-, and 4-methyldecaboranes behaved as weak acids in potentiometric titrations in acetonitrile.[619]

Although earlier workers[727] did not find decaborane to react further with the bases sodium hydride or sodium hydroxide in ether, later workers found that at least 1·2 moles of hydrogen per mole of decaborane could be evolved[734]; recent workers have shown that decaborane behaves as a diprotic acid towards sodium hydride in diethylether, and were able to isolate and characterize the ether-insoluble salt $Na_2B_{10}H_{12}$.[735–7]

n- AND *i*-OCTADECABORANE(22)

Both *normal*- and *iso*-$B_{18}H_{22}$ ionize in water to yield the corresponding mono- and di-basic acids[297]:

$$n\text{- or } i\text{-}B_{18}H_{22} \overset{H_2O}{\rightleftharpoons} n\text{- or } i\text{-}B_{18}H_{21}^- \rightleftharpoons n\text{- or } i\text{-}B_{18}H_{20}^{2-}$$

Reactions with *n*-butyl lithium evolve butane leading to the salt:

$$2BuLi + B_{18}H_{22} \rightarrow 2BuH + B_{18}H_{20}^{2-} + 2Li^+$$

E. Electron Addition Reactions

(i) DIRECT ADDITION OF ELECTRONS

Pentaborane(9)

The chemistry of the pentaborane–metal salts has been reviewed.[738] Stock[32] had reported that potassium amalgam reacts with pentaborane(9) to form $K_2B_5H_9$ although this compound was not structurally characterized. The reaction of pentaborane(9), dissolved in liquid ammonia and stored for several days[739], with lithium yielded a product $Li_2B_5H_9(NH_2)_2$ which however was not completely characterized. Ford and co-workers found no reaction between sodium amalgam or sodium hydride and pentaborane(9) in ether at room temperature.[716–17] The reaction of potassium with pentaborane(9) in tetrahydrofuran may produce KB_8H_{13} as one of the products.[740]

Pentaborane(11)

The reaction of B_5H_{11} with alkali metals is complicated by the decomposition of the hydride in ether solvent, and some $B_3H_8^-$ is produced.[716–17]

Octaborane(12)

Ethereal solutions of B_8H_{12} react with sodium amalgam to produce a salt which analyzes approximately as containing an ion of empirical formulation $B_8H_{12}^-$.[132–3]

Decaborane(14)

$B_{10}H_{14}$ reacts with alkali metals in ethers[721, 738], benzene[741] or liquid ammonia[742–5] to produce eventually the $B_{10}H_{14}^{2-}$ ion as the major species. At an intermediate stage in the reaction in ethers, a deep red solution is formed which has been attributed to the $\cdot B_{10}H_{14}^-$ radical anion. A further by-product of the reaction is the $B_{10}H_{13}^-$ ion. Patents have also been issued for the products of reaction of lithium with decaborane in tetrahydrofuran[746], and magnesium with decaborane in liquid ammonia.[747]

The mechanism of the electrolytic reduction of decaborane has been examined using electrochemical, e.s.r. and electronic spectroscopic methods.[748–9, 750, 750a] The first reduction step involves a one-electron transfer to decaborane(14) to produce a radical ion, which then undergoes a rapid first-order decay to a more stable radical ion, which then appears to disproportionate to $B_{10}H_{13}^-$ and $B_{10}H_{15}^-$. The second step[751] originates from a one-electron reduction of $B_{10}H_{13}^-$. The resulting radical dianion $\cdot B_{10}H_{13}^{2-}$ rapidly disproportionates to form $B_{10}H_{14}^{2-}$ and $B_{10}H_{12}^{2-}$ which react rapidly with bulk $B_{10}H_{14}$ to regenerate more electroactive $B_{10}H_{13}^-$. This reaction sequence corresponds to:

$$4B_{10}H_{14} + 6e^- \rightleftharpoons B_{10}H_{12}^{2-} + B_{10}H_{14}^{2-} + 2B_{10}H_{15}^-$$

A reaction between $B_{10}H_{15}^-$ and $B_{10}H_{12}^{2-}$ over the longer time scale involved in controlled-potential electrolysis generates $B_{10}H_{13}^-$, so that the net reaction under these conditions is:

$$B_{10}H_{14} + 2e^- \rightleftharpoons B_{10}H_{14}^{2-}$$

Although it may not be safe to apply the mechanisms found in electrolytic reductions to those reductions involving metal amalgams, it is apparent that similar species are present, and the reasons for their production may be similar.

n- and i-Octadecaborane(22)

The reactions of *n*- and *i*-$B_{18}H_{22}$ with sodium amalgam have been examined, and a two-electron addition observed[297]:

$$n\text{- or } i\text{-}B_{18}H_{22}+2e^- \xrightarrow{\text{Na/Hg}} n\text{- or } i\text{-}B_{18}H_{22}^{2-}$$

A transient green colour in the reaction may have been due to the initial formation of the radical anion $\cdot B_{18}H_{22}^-$.

(ii) ANIONIC ELECTRON DONORS

The kinetics and mechanism for acid–base reactions involving boranes have been reviewed.[752]

Pentaborane(9)

B_5H_9 is reported[753] to react with sodium cyanide to form the $B_5H_9CN^-$ ion.

Decaborane(14)

$B_{10}H_{14}$ also reacts with sodium cyanide in ethers at 25° to form initially a coloured species $[NaB_{10}H_{14}CN]$ which then decomposes with hydrogen evolution:

$$NaCN+B_{10}H_{14} \xrightarrow[R_2O]{25^\circ} [NaB_{10}H_{14}CN] \xrightarrow{0\text{–}25^\circ} NaB_{10}H_{12}CN+H_2$$

By this route, $NaB_{10}H_{12}CN,2Et_2O$, $NaB_{10}H_{12}NCO,2{\cdot}5C_4H_8O_2$, $Me_4NB_{10}H_{12}SCN$, $NaB_{10}H_{12}OMe,C_4H_8O_2$ and $Me_4NB_{10}H_{12}C(CN)_3$ were prepared.[753] A patent involving in principle the reactions of alkali-metal or tetraalkylammonium salts of a variety of univalent pseudo-halogen types of anion with decaborane(14) has been claimed.[754] The reaction of decaborane with strong bases as mentioned in subsection D may in fact proceed through the initial formation of an adduct of the basic anion. It has already been mentioned that n.m.r. evidence shows that the $B_{10}H_{15}^-$ ion is an intermediate in the attack of the borohydride ion on decaborane.[728] Furthermore, the $B_{10}H_{14}^{2-}$ ion is formed when decaborane(14) is treated with BH_4^- in aqueous solution.[162]

The interaction of beryllium borohydride and its etherate with decaborane has been discussed.[755]

(iii) NEUTRAL ELECTRON DONORS

Pentaborane(9)

The reactions between Group V or VI neutral ligands with B_5H_9 are in general complicated by cleavage, as already mentioned. At low temperatures the reaction of amines with pentaborane(9) results in adducts. Thus Stock[32] reported that ammonia reacted to produce $B_5H_9,4NH_3$, and Schlesinger[739, 756–7] found that the reaction needed three days for completion at −63 to −80°. A more recent reinvestigation[758] found a loosely bound diammonia adduct at −80°, and that the ammonia could be removed by pumping at −65° to −45°:

$$2NH_3+B_5H_9 \xrightarrow[18\text{–}72\text{ hr}]{-80^\circ} B_5H_9,2NH_3 \xrightarrow[\text{Vacuum}]{-65^\circ} B_5H_9+2NH_3$$

Incompletely characterized adducts were also formed at room temperature in ether or hydrocarbon solvents.[705, 759] The reactions of pentaborane(9) with alkylamines are complicated by cleavage. Partial reversibility at −80° has been observed for the trimethylamine–pentaborane(9)[702] and dimethylamine–pentaborane(9) systems.[698] Aromatic amines such as aniline, methylaniline, dibenzylamine, pyridine, 2-amino-pyridine, quinoline and diphenylamine[708, 760–3] in general react with pentaborane(9) to form 2:1 and 3:1 adducts. Similar adducts are found with ethylenediamine.[708, 762] N,N,N′,N′-tetramethylethylenediamine (TMED) reacted with pentaborane(9) to give B_5H_9,TMED which was converted by MeOH at 0° to B_4H_8,TMED.[764] MeCN reacted with pentaborane(9) to give incompletely characterized products for which the formulae $B_5H_6,3MeCN$[765] and $B_5H_9(MeCN)_5$[763, 766] were suggested. The $B_5H_9,2Me_3N$ adduct reacted with isotopically enriched diborane to regenerate B_5H_9 and give Me_3N,BH_3 each of which contained the isotopically labelled boron atoms.[767] The reaction of pentaborane(9) with hydrazine in the gas phase was reported to give a non-volatile liquid of composition $B_5H_9,9N_2H_4$.[768–70] Other workers[771–2] found a diadduct $B_5H_9,2N_2H_4$, whereas the reaction in ether was reported to give $B_5H_9,2{\cdot}5N_2H_4$ or $B_5H_9,5N_2H_4$[773], but efforts to obtain a stable product from the reaction in benzene were unsuccessful. The stoichiometric reaction was presented as a Mollier diagram which plots enthalpy versus entropy for the system[774] and recent workers[775–7] found that pentaborane and hydrazine react in a 1:2 ratio in dilute cyclohexane by a first-order process yielding an insoluble adduct and hydrogen:

$$B_5H_9 + 2N_2H_4 \rightarrow B_5N_4H_{16} + 0{\cdot}5H_2$$

The reaction between N_2D_4 and B_5D_9 has been patented as an explosive device.[778]

When monomethylhydrazine and unsymmetrical dimethylhydrazine were used, the reactions were respectively:

$$B_5H_9 + 4MeNHNH_2 \rightarrow B_5N_8H_{20}Me_4 + 0{\cdot}5H_2$$
$$B_5H_9 + 2H_2NNMe_2 \rightarrow B_5N_4H_{13}Me_4$$

The products were thought to be polymeric, but attempts to obtain definitive structures were unsuccessful.[776] Pentaborane(9) did not give an isolable product from the reaction with ethyl sulphide[762], nor any observable reaction up to 80° with methyl sulphide.[763]

Pentaborane(11)

The reaction of bases with B_5H_{11} usually results in cleavage, although the intermediate $B_5H_{11}(Me_2O)_2$ was reported from the reaction with dimethyl ether.[261, 504]

Hexaborane(10)

B_6H_{10} has been reported to react with triphenylphosphine to give the adduct B_6H_{10},PPh_3.[52]

Octaborane(12)

B_8H_{12} is a strong monobasic Lewis acid, and several compounds of the type B_8H_{12},L have been prepared. Thus, reaction with ether produced $B_8H_{12}(OEt_2)_{1{\cdot}04}$, and reactions with trimethylamine and acetonitrile gave respectively B_8H_{12},NMe_3 and $B_8H_{12},NCMe$.[132–3]

i-Nonaborane(15)

When a toluene solution of *i*-B_9H_{15} was treated with excess of MeCN, a quantitative yield of $B_9H_{13},MeCN$ was recovered from the reaction mixture.[142] Treatment of MB_9H_{14} with hydrogen chloride in ether produced the derivative B_9H_{13},OEt_2 from which other B_9H_{13},L derivatives could be obtained.[474]

Decaborane(14)

$B_{10}H_{14}$ reacts with a wide variety of basic ligands such as amines, phosphines, sulphides, phosphine oxides, sulphoxides, amides, nitriles, isonitriles, thioureas and others to form a series of derivatives of the type $B_{10}H_{12}L_2$ by the reaction:

$$2L + B_{10}H_{14} \rightarrow B_{10}H_{12}L_2 + H_2$$

These compounds are best regarded as formal derivatives of the $B_{10}H_{14}^{2-}$ ion, and will be discussed in detail in Part 8. The mechanism of the formation of these compounds is undoubtedly complex. Beachell and Dietrich examined kinetically the reactions involving substituted anilines[779] and symmetrical diethylthiourea[780–2], and found the rate expression to be first order with respect to both the ligand and a ligand–$B_{10}H_{14}$ complex:

$$d[H_2]/dt = k_2[\text{complex}][\text{ligand}]$$

When the less nucleophilic nitriles were used as ligands, the rate-determining transition state was composed of nitrile and $B_{10}H_{14}$[783]:

$$d[H_2]/dt = k_2[B_{10}H_{14}][RCN]$$

Although the reaction scheme below is compatible with the kinetic results for the aniline reactions:

$$B_{10}H_{14} + PhNH_2 \xrightarrow{\text{fast}} B_{10}H_{13}^{-}PhNH_3^{+}$$
$$B_{10}H_{13}^{-}PhNH_3^{+} + PhNH_2 \xrightarrow{\text{slow}} B_{10}H_{13}PhNH_2^{-} + PhNH_3^{+}$$
$$B_{10}H_{13}PhNH_2^{-}\,PhNH_3^{+} \xrightarrow{\text{fast}} B_{10}H_{12}(PhNH_2)_2 + H_2$$

the kinetics of the nitrile system are more compatible with a reaction involving the initial formation of a substituted $B_{10}H_{15}^{-}$ ion:

$$B_{10}H_{14} + RCN \xrightarrow{\text{slow}} B_{10}H_{14},RCN$$
$$B_{10}H_{14},RCN \xrightarrow{\text{fast}} B_{10}H_{12},RCN + H_2$$
$$B_{10}H_{12},RCN + RCN \xrightarrow{\text{fast}} B_{10}H_{12}(RCN)_2$$

However, the reaction of decaborane with ammonia has been investigated several times. Stock[32] found reversible addition of 6 moles of NH_3 at −75°, and Toeniskoetter et al.[476,743,744] demonstrated the existence of tri-, tetra- and hexa-ammoniates. More recently, ammonia has been shown to react with decaborane in benzene to give a 'triammoniate' which has the structure $NH_4^+[B_{10}H_{13}NH_3,NH_3]^-$[784], and thus supports the work of Beachell et al. On heating to 75–95°[784], or by heating ammonia and decaborane at 110°[785–6], the compound $B_{10}H_{12}(NH_3)_2$ was formed. Other work has been reviewed by Holzmann[24], and $B_{10}H_{12}(NH_3)_2$ has been prepared by the reaction of $B_{10}H_{14}$ with ammonia in ether.[787]

Octadecaborane(22)

No reaction was found[297] between $B_{18}H_{22}$ and MeCN on refluxing for 5 days, although triethylamine reacts to form $Et_3NH^+B_{18}H_{21}^-$.

Icosaborane(16)

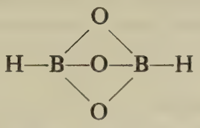
$B_{20}H_{16}$ reacts with a variety of Lewis bases to give adducts[89], although structural rearrangement also occurs.[90,92] Examples of the compounds formed include $B_{20}H_{16}(OEt_2)_2$, $B_{20}H_{16}(NMe_3)_2$, $B_{20}H_{16}(PEt_3)_2$ and $B_{20}H_{16}(SMe_2)_2$. With protonic Lewis bases such as water and ethanol, ionization occurs to yield, e.g., the ions $B_{20}H_{16}(OH)_2^{2-}$ and $B_{20}H_{16}(OEt)_2^{2-}$.

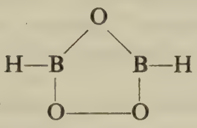
F. Oxidation

The combustion of the boron hydrides has been reviewed.[788]

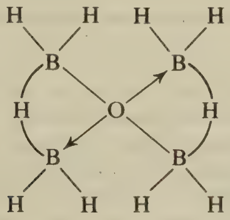
PENTABORANE(9)

The ultimate oxidation of pentaborane(9) yields boric oxide and water, but the difficulty of obtaining a quantitative reaction makes it unsatisfactory for calorimetric work. Pentaborane(9) may sometimes be exposed to the air without vigorous reaction, although it may inflame spontaneously or even detonate under suitable conditions[789]; the spontaneous ignition limits of pentaborane–air mixtures have been determined.[790] The explosive oxidation of the boranes has been reviewed and critical temperatures and pressures obtained for mixtures of oxygen and pentaborane(9).[791–2] Low concentrations (1–2%) of pentaborane(9) in air or air–nitrogen mixtures yield self-sustaining flames, and the presence of moisture has no effect on the flammability limits.[793–4] Mixtures of pentaborane(9) and oxygen at and below the first pressure limit of explosion undergo a luminous reaction with deposition of a white solid on the walls of the container.[793] The mechanism and chemical inhibition of the oxidation reaction have been studied.[795] The use of iron carbonyl, tetraethyllead and the products of oxidation for inhibition has been reported.[789, 796-7] The products of the partial oxidation of B_5H_9 have been shown to include diborane, hydrogen[791, 796-7], and a white solid which has been 'identified' as $B_4H_{12}O$, $B_2H_2O_3$ or both.[798] Of the two alternative structures for $B_2H_2O_3$, the evidence obtained by Ditter and Shapiro[798] indicated structure (I), although recent workers have


(I)


(II)

reinvestigated this and decided in favour of structure (II)[799a-c], and others[800-1] have questioned its existence, proposing instead μ-oxidobis(diborane), $B_4H_{10}O$:



Kinetic study of the reaction of atomic oxygen with pentaborane(9) has been reported.[802] The mechanism proposed to account for the experimental observations is:

$$\begin{aligned} O + B_5H_9 &\longrightarrow B_5H_9O \\ B_5H_9O + B_5H_9 &\longrightarrow (B_5H_9OB_5H_9) \\ (B_5H_9OB_5H_9) &\longrightarrow B_5H_9O + B_5H_7 + H_2 \\ B_5H_9O &\xrightarrow{\text{wall}} B_5H_7O + H_2 \end{aligned}$$

Two processes can account for the fate of the B_5H_7 fragments:

$$B_5H_7 + B_5H_9 \longrightarrow B_{10}H_{14} + H_2$$

and
$$2B_5H_7 \xrightarrow{\text{wall}} B_{10}H_{14}$$

No traces of diborane or $H_2B_2O_3$ were found in the reaction.

The burning properties and flame speeds of pentaborane–oxygen–nitrogen mixtures have been studied[803-5], and the relative fuel-flow requirements of pentaborane(9) in the ramjet system have been reported as part of a review on the combustion of boron hydrides.[806] The effect of inlet air temperature and combustion pressures on the ramjet combustion performance of pentaborane mixtures has been described.[807] Stahl has also described the combustion properties of pentaborane(9)[808], and pentaborane–air flame and explosions have been studied spectroscopically.[804]

The prevention of pentaborane fires and explosions in air by chemical techniques has been investigated by diffusion and by shock-tube techniques.[809] The application of B_5H_9 in high-energy fuels has been extensively studied.[30, 810-20] The use of B_5H_9 in welding has also been mentioned.[821]

No detailed behaviour under oxidation has been reported for the less readily available hydrides, e.g. B_5H_{11}, B_6H_{10}, B_6H_{12}, B_8H_{12}, B_8H_{14}, B_8H_{18} and *n*- and *i*-B_9H_{15}. However, owing to their latent instability—with the possible exception of hexaborane(10)—all will be extremely easily oxidized, if not spontaneously inflammable in air.

Decaborane(14)

Stock[32] found that at room temperature decaborane is stable to air, but that it explodes with oxygen at about 100°. The explosive limits of decaborane–oxygen mixtures were found to be rather erratic in the temperature range 80–120°, and at oxygen:decaborane ratios of less than 11:1, explosions occurred before the decaborane could be vaporized.[791] The oxidation behaviour of decaborane has been reported by Holzmann[822], and the explosive reaction of decaborane–oxygen mixtures has been studied.[823] The use of decaborane(14) with a range of oxidants as a solid propellant has been reported.[824]

n- AND *i*-OCTADECABORANE(22) AND ICOSABORANE(16)

These hydrides are air-stable at room temperature, and no data are available for detailed oxidations.

An order of reducing ability of the hydrides $B_4H_{10} > B_2H_6 > B_5H_9 > B_{10}H_{14}$ has been suggested on the basis of an equilibrium tension pH study.[825]

G. Hydrolysis, Alcoholysis and Reactions with Mercaptans

PENTABORANE(9)

The reaction of pentaborane(9) with cold water was reported by Stock[32] to be very slow, and in 30% sodium hydroxide pentaborane(9) dissolved with almost no gas evolution. When the solution was acidified, hydrogen was released but the hydrolysis was not complete for several days. The slow hydrolysis was explained by immiscibility with water, since the hydrolysis in dioxan is very fast.[826–7] The vapour-phase hydrolysis was investigated at 85° and 150°, and a mechanism for the reaction proposed[828]; the kinetics of the vapour phase hydrolysis have also been studied.[829]

The methanolysis of pentaborane(9) goes nearly to completion overnight at room temperature, although excess of pentaborane leads to traces of dimethoxyborane and methoxyborane.[789] Similar formations of B–H bonds which can be further alcoholyzed have been reported.[830–1] Ethyl and butyl mercaptan cleave pentaborane with hydrogen liberation to yield tris(alkylmercapto)boranes.[832]

PENTABORANE(11)

B_5H_{11} is quantitatively hydrolyzed to tetraborane(10), boric acid and hydrogen[489]:

$$B_5H_{11} + 3H_2O \rightarrow B_4H_{10} + B(OH)_3 + 2H_2$$

HEXABORANE(10) AND HEXABORANE(12)

Stock has reported[32] that B_6H_{10} does not completely hydrolyze in 16 hr with water at 90°. Reaction with 30% alkali liberates very little hydrogen, but acidification causes immediate complete hydrolysis. B_6H_{12} behaves similarly to B_5H_{11} with water, in that it is hydrolyzed to tetraborane(10)[126]:

$$B_6H_{12} + 6H_2O \rightarrow B_4H_{10} + 2B(OH)_3 + 4H_2$$

n- and *i*-OCTABORANE(12) AND OCTABORANE(14)

B_8H_{12} is quantitatively hydrolyzed by water in diethyl ether solution to form B_6H_{10} by the reaction[132–3]:

$$B_8H_{12} + 3H_2O \xrightarrow{Et_2O} B_6H_{10} + B_2O_3 + 4H_2$$

Hydrolysis of B_8H_{14} was complete after heating a sample with water at 100° for 24 hr.[132–3]

i-NONABORANE(15)

A sample of *i*-B_9H_{15}, treated with excess of methanol, was completely methanolized after 9 hr at 100°.[143]

DECABORANE(14)

$B_{10}H_{14}$ is quantitatively hydrolyzed by water only at 200°. At room temperature hydrolysis is only about 10% complete in 10 days. Atteberry has studied the kinetics of the hydrolysis of decaborane[833], and the hydrolytic behaviour has been described.[822] The acidic character of decaborane has already been described in subsection D (above).

Decaborane reacts with alcohols and mercaptans[834], and with a variety of other common organic solvents, e.g. ethers, organic halogen and nitro-compounds, amides, nitriles and ketones. The behaviour of decaborane(14) in organic solvents has been reported.[835] Kinetic studies of the reaction of decaborane with alcohols have been made[836–8]; for the primary alcohols the observed variations of the rate constant with the number of carbon atoms and dielectric constant of the medium are consistent with the Kirkwood formula. For substituted alcohols, the greater the availability of the electrons on oxygen, the more rapidly the reaction occurs.

Curious alkoxylations occur in the reactions of $NaB_{10}H_{13}$ with iodine in ethers to form $B_{10}H_{13}OR$ compounds.[725, 839]

n- AND *i*-OCTADECABORANE(22)

Both *n*- and *i*-$B_{18}H_{22}$ are reversibly ionized in water and this has been previously discussed (subsection D, above).

ICOSABORANE(16)

$B_{20}H_{16}$ dissolves irreversibly in water to form a strongly acidic solution[87, 89], which contains the species $(H_3O^+)_2B_{20}H_{16}(OH)_2^{2-}$. Similarly, with alcohol, the $B_{20}H_{16}(OEt)_2^{2-}$ ion is formed.

H. Other Chemical Reactions

The B_2D_6/B_5H_9 exchange reaction has been studied by mass-spectrometry[840], infra-red spectroscopy[841] and n.m.r. spectroscopy.[842] The results indicate that no boron exchange occurs up to the decomposition temperature of pentaborane(9)[843], and that hydrogen exchange occurs at the terminal positions. The H-exchange reaction was found to be of first-order in B_5H_9 and half-order in B_2H_6[844], suggesting that the exchange reactions occur via BD_3 and B_5H_9, and the corresponding B_2H_6/B_5D_9 reaction is slower in accordance with the normal isotope effect.[845–6] Boron exchange in the B_2H_6/B_5H_9 reaction could be effected by the use of alumina catalysts.[847] Hillman and co-workers have studied the reaction between diborane and pentaborane(9) by isotopic labelling, and have found that the reaction to produce $B_{10}H_{14}$ involves both B_5H_9 and B_2H_6[848–50]:

$$^{11}B_5H_9 + 2{\cdot}5\,^{10}B_2H_6 \rightarrow {}^{11}B_5{}^{10}B_5H_{14} + 5H_2$$

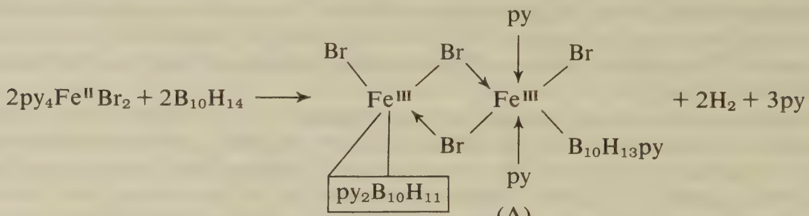
Hydrogen-arc photolysis of pentaborane(9) probably produces decaborane(14).[851] B_5H_9 has also been reported to catalyze the conversion of dimeric dimethylaminoborane to the trimeric form.[706] The reactions of pentaborane which are radiation-induced have also been discussed.[852]

A study of the isotopic exchange of deuterium and ^{10}B between diborane and pentaborane(11) has shown that the reaction is homogeneous. The exchange was half-order for B_5H_{11} and first-order for B_2H_6. All the boron and hydrogen atoms in both reactants participated in the exchange, and the following equilibrium was suggested[853–5]:

$$B_5H_{11} \rightleftharpoons B_4H_8 + BH_3$$

An infra-red study of the exchange of deuterium between decaborane(14) and diborane has shown that not all the hydrogen atoms of decaborane participate in the reaction.[856] Diborane reacts with decaborane(14) at 100° to form a yellow solid which is soluble in excess decaborane.[857]

An unusual reaction in which decaborane acts as an oxidizing agent has recently been reported[858]: decaborane oxidizes an equimolar quantity of $py_4Fe^{II}Br_2$ in boiling benzene with liberation of hydrogen and precipitation of a light-brown compound which has been assigned the structure (A):



(A)

Tetrahydrofuran cleaves (A) to give an insoluble complex $pyFe^{III}Br_2B_{10}H_{11}py_2$ and a brown, THF-soluble monomeric compound of tetrahedral, high-spin iron(III), $pyFe^{III}Br_2B_{10}H_{13}py$.

^{60}Co γ-ray radiolysis of decaborane(14) produces hydrogen, diborane, pentaborane(9) and polymeric substances[859], while acetals and ortho-esters react with it to yield a variety of products including borates and polymeric materials.[860]

Cyclic ethers react with decaborane to give polymeric products.[861] Cellulose and cellulose derivatives react with decaborane(14) to incorporate it into single-base and double-base matrices.[862]

The decomposition of boron hydrides when heated into elemental boron and hydrogen has been used to give boron coatings on surfaces[863], and as an analytical technique.[864]

PART 7: PREPARATIONS AND PHYSICAL PROPERTIES OF HYDRIDE ANIONS

A. Preparation of Hydride Anions

1. *Closo*-POLYHEDRAL SPECIES

Historically, the first polyhedral ions to be prepared were the decahydro-*closo*-dodecaborate(2–) ion, $B_{10}H_{10}^{2-}$, and the dodecahydro-*closo*-dodecarborate(2–) ion $B_{12}H_{12}^{2-}$; the latter was obtained by treating 2-iododecaborane(14) with triethylamine.[865–6] Four general routes to the polyhedral ions have now been developed, namely via: (a) B–H condensation reactions (b) pyrolysis of polyhedral and *nido*-borane (open-structured) ions (c) degradative methods and (d) displacement reactions on $B_{10}H_{12}L_2$ compounds.

(a) *B–H Condensations*

The reactions of the tetrahydroborate(1 –) ion with boron hydrides can be generalized as follows[25]:

$$2BH_4^- + B_xH_y \rightarrow [(2+x)/n]B_nH_n{}^{2-} + [(y-x+6)/2]H_2$$

Thus the $B_6H_6^{2-}$ ion was prepared[39] by passing diborane into a diglyme solution of $NaBH_4$ at 100° and refluxing the resulting solution at 162° for 16 hr. The $B_{12}H_{12}^{2-}$ ion was similarly prepared from the reaction between diborane and sodium tetrahydroborate using triethylamine as solvent at 180°[678–9], or in diglyme solution at the same temperatures.[867–8] The reaction also proceeds with sodium tetrahydroborate and other boron hydrides[678–9, 680], for example:

$$2NaBH_4 + B_{10}H_{14} \rightarrow Na_2B_{12}H_{12} + 5H_2$$

Alternatively, a variety of ligand–borane adducts may be used instead of the tetrahydroborate[678–681]:

$$2Et_3NBH_3 + 5B_2H_6 \xrightarrow{180^\circ} (Et_3NH)_2B_{12}H_{12} + 11H_2$$
$$2Et_3NBH_3 + B_{10}H_{14} \longrightarrow (Et_3NH)_2B_{12}H_{12} + 3H_2$$

During the course of these reactions side-products can be formed if weak bases such as phosphines, arsines or sulphides are used, or if there is little steric hindrance with the base used. For example phosphines and arsines give rise to compounds of the type $B_{12}H_{11}L^-$ and the very weak and relatively unhindered base Me_2S gives $B_{12}H_{10}(SMe_2)_2$ as the major product. This general method has been used to prepare $B_{12}H_{12}^{2-}$ on an industrial scale.[869]

The $B_{10}H_{10}^{2-}$ ion is probably an intermediate in the condensation reactions which give rise to $B_{12}H_{12}^{2-}$, and although the best conditions for its formation have probably not yet been found[42, 53], lower reaction temperatures than those used in forming $B_{12}H_{12}^{2-}$ favour $B_{10}H_{10}^{2-}$ yields.

A number of patents have been issued relevant to the above reactions.[870-5]

(b) *Pyrolysis of Hydride Anions*

Pyrolysis of Et_4NBH_4 at 185° led to high yields of $B_{10}H_{10}^{2-}$ [876], although the tetramethylammonium salt under similar conditions yielded only Me_3NBH_3 and methane. Pyrolysis of $Et_4NB_3H_8$ also led to $B_{10}H_{10}^{2-}$, while the Me_4N^+ salt gave an equimolar mixture of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ [876], and the potassium and cæsium salts gave complex mixtures containing BH_4^-, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$.[867, 876] Other workers have also isolated $B_9H_9^{2-}$ from pyrolysis of CsB_3H_8.[53]

Similar results may be obtained by pyrolyzing salts of $B_9H_{14}^-$, $B_{10}H_{14}^{2-}$, $B_{10}H_{15}^-$, or $B_{10}H_{12}^{2-}$. The pyrolysis of $Cs_2B_{11}H_{13}$ at 250° led to high yields of $Cs_2B_{11}H_{11}$, although pyrolysis of the double salts $Cs_2B_{11}H_{13}$,CsCl and $Cs_2B_{11}H_{13}$,$CsBH_4$ led instead to mixtures of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, while the $B_{11}H_{11}^{2-}$ ion itself could be converted to an equimolar mixture of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ by pyrolysis.[53]

(c) *Degradation methods*

Oxidative degradation of hydrated $B_9H_9^{2-}$ salts in ethanol, tetrahydrofuran or 1,2-dimethoxyethane solutions led to the species $B_8H_8^{2-}$, $\cdot B_8H_8^-$, $B_7H_7^{2-}$ and $B_6H_6^{2-}$.[42]

(d) *Ligand-Displacement Reactions*

Derivatives of the type $B_{10}H_{12}L_2$ in which L is a weak ligand such as SMe_2 react with strong bases to form $B_{10}H_{10}^{2-}$ [57, 865-6], or alternatively decaborane reacts with triethylamine:

$$B_{10}H_{12}(Me_2S)_2 + 2NH_3 \rightarrow (NH_4)_2B_{10}H_{10} + 2Me_2S$$
$$B_{10}H_{14} + 2Et_3N \rightarrow B_{10}H_{12}(Et_3N)_2 + H_2 \rightarrow (Et_3NH)_2B_{10}H_{10}$$

Bases other than amines may be used.

The mechanism of the formation of the $B_{10}H_{10}^{2-}$ ion has been studied kinetically and by using selectively deuterated starting materials.[879-83]

The reaction to form $B_{10}H_{10}^{2-}$ by treating a variety of $B_{10}H_{12}(\text{Ligand})_2$ compounds with triethylamine was shown to be of first order in $B_{10}H_{12}(\text{Ligand})_2$, and independent of triethylamine concentration at high concentrations. The steps suggested were:

$$B_{10}H_{12}(\text{Ligand})_2 \rightleftharpoons B_{10}H_{12}(\text{Ligand}) + \text{Ligand}$$
$$B_{10}H_{12}(\text{Ligand}) + NEt_3 \rightarrow B_{10}H_{11}^- + HNEt_3^+ + \text{Ligand}$$
$$B_{10}H_{11}^- + NEt_3 \rightarrow B_{10}H_{10}^{2-} + HNEt_3^+$$
$$B_{10}H_{12}(\text{Ligand}) + NEt_3 \rightarrow B_{10}H_{12}(\text{Ligand})NEt_3$$
$$B_{10}H_{12}(\text{Ligand}) \rightarrow \text{Unidentified products}$$

Patents which have been issued on the $B_{10}H_{10}^{2-}$ ion include refs. 884–8, and synthetic details have also been reported for $(Et_3NH^+)_2B_{10}H_{10}^{2-}$.[889] Experimental details of the preparations of $B_8H_8^{2-}$, $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$ have been given.[889a]

2. '*Nido*' OR OPEN BORON-HYDRIDE ANIONS

The general methods for obtaining the borane anions include: (e) treating a borane or a derivative with a basic reagent such as H^-, BH_4^-, OH^-, (f) treating a boron hydride with an electron donor, e.g. Na/Hg, and (g) degradative methods.

(e) *Treatment of a Borane or Derivative with a Base*

The $B_5H_8^-$ ion has been prepared by treating pentaborane(9) with NaH or KH, or Li alkyls[106,472,591,718], and the $B_6H_9^-$ ion has been prepared by treating B_6H_{10} with methyllithium, sodium hydride, or potassium hydride.[117,720]

An ion of empirical formula $B_8H_{12}^-$ has been prepared by treating B_8H_{12} with sodium hydride[132–3], and the $B_9H_{12}^-$ ion has been prepared by treating diethylsulphide-nonaborane(13) with strong bases[645]:

$$B_9H_{13}L + Me_4N^+OH^- \rightarrow Me_4N^+B_9H_{12}^- + H_2O + L$$

A number of workers have reported the preparation of the $B_{10}H_{13}^-$ ion by treating decaborane with basic reagents.[721–3,726–8] The bases used include H^-, OH^-, OCH_3^-, $BH(OCH_3)_3^-$, BH_4^-, and these have already been discussed (Part 6, D).

Decaborane 'Grignard' reagents have been prepared by treating $B_{10}H_{14}$ with RMgX in ether solutions, and the products behave as $B_{10}H_{13}^-$ and $B_{10}H_{12}^{2-}$ species.[638–9] The $B_{10}H_{12}^{2-}$ ion has also been prepared by the extended reaction of decaborane with excess of sodium hydride.[735–7]

The reaction of aqueous BH_4^- with decaborane(14) has led to the $B_{10}H_{14}^{2-}$ ion[162], and the $B_{10}H_{15}^-$ ion has been shown to be an intermediate in the reaction in ether solution.[728] The $B_{10}H_{15}^-$ ion has also been prepared by the reversible protonation of $B_{10}H_{14}^{2-}$.[160]

The $B_{11}H_{14}^-$ ion has been prepared by treating decaborane(14) or diborane with BH_4^- in dioxane at 80°[169], and the $B_{11}H_{13}^{2-}$ ion may be obtained from it by proton abstraction with a strong base.

The normal and *i*-$B_{18}H_{21}^-$ and $B_{18}H_{20}^{2-}$ ions have been obtained from aqueous ionization of *n*- and *i*-$B_{18}H_{22}$.[279,297]

(f) *Direct Electron-Addition to a Boron Hydride*

The ion of empirical composition $B_8H_{12}^-$ has been obtained by treating B_8H_{12} with Na/Hg.[132–3] As discussed in Part 6, E, the direct electron addition to decaborane(14) leads to the formation of $B_{10}H_{13}^-$, $\cdot B_{10}H_{14}^-$ and $B_{10}H_{14}^{2-}$. The reaction of Na/Hg with *n*- or *i*-$B_{18}H_{22}$ results in the formation of *n*- or *i*-$B_{18}H_{22}^{2-}$.[297]

Treatment of $B_{10}H_{14}$ with calcium in liquid ammonia gives the compound $CaB_{10}H_{14}6NH_3$.[890]

(g) *Degradative Methods*

Decaborane(14) is degraded in aqueous bases to form boric acid, hydrogen and the $B_9H_{14}^-$ ion[713]:

$$B_{10}H_{14} + 1 \text{ mole equivalent aq. KOH or NaOH} \xrightarrow{12\,\text{hr}} H_2 + B_9H_{14}^-$$

$B_{10}H_{14}$ and 2 mole equivalents of aqueous base react quickly to give a colourless, reasonably stable intermediate which is slowly hydrolyzed to the $B_9H_{14}^-$ ion, or is rapidly hydrolyzed on acidification to give the $B_9H_{14}^-$ ion in good yield. The following reaction scheme was proposed:

$$B_{10}H_{14} + OH^- \rightarrow B_{10}H_{13}^- + H_2O$$
$$B_{10}H_{13}^- + OH^- \rightarrow B_{10}H_{13}OH^{2-}$$
$$B_{10}H_{13}OH^{2-} + H_3O^+ + H_2O \rightarrow B_9H_{14}^- + B(OH)_3 + H_2$$

Evidence for the presence of an intermediate solvated $B_{10}H_{13}^-$ species has been found in the reaction of decaborane with aqueous ammonia.[891]

A derivative of the hypothetical $B_8H_{13}^-$ ion has been prepared by treating $EtNH_2,B_9H_{13}$ with ethylamine[645]; its structure was first established by *X*-ray examination.[136–8]

3. LINKED POLYHEDRAL IONS

(h) *Oxidative Coupling*

The $B_{10}H_{10}^{2-}$ ion reacts in aqueous solution with oxidizing agents such as Fe^{3+} or Ce^{4+} to yield as a final product the $B_{20}H_{18}^{2-}$ ion.[186–7,892] An early publication[893] on

$B_{20}H_{18}^{2-}$ was later corrected. Intermediates in the reaction were $B_{20}H_{19}^{3-}$ and the double salt $B_{20}H_{18}^{2-}, B_{20}H_{19}^{3-}(Et_3NH^+)_5$. The oxidation can also be effected electrochemically.[893a, 894] The $B_{20}H_{19}^{3-}$ ion can be isolated from the products of the direct reaction of Ce^{4+} with $B_{10}H_{10}^{2-}$ at 0°[187, 895], or by reduction of the $B_{20}H_{18}^{2-}$ ion with active metals such as magnesium, aluminium or zinc. It can also be prepared in high yield by the two-phase reaction of very concentrated solutions of $B_{10}H_{10}^{2-}$ and Fe^{3+}.[896] Reduction of $B_{20}H_{18}^{2-}$ with sodium in liquid ammonia yields the equatorial–equatorial isomer. This was successively converted by acid catalysis to the axial–equatorial and axial–axial isomers.[187, 895] The reduction could also be carried out with zinc and acid although the product appears to be a mixture of isomers.[186] The $B_{20}H_{18}^{4-}$ ions protonate to yield only one stable isomer of $B_{20}H_{19}^{3-}$.

Electrochemical oxidation of $B_{12}H_{12}^{2-}$ has yielded the $B_{24}H_{23}^{3-}$ ion.[199, 894]

Table 7.1.—Synthesis of Boron Hydride Anions: Summary

Type of ion	Species	Method of preparation
Simple *closo*-polyhedral ions	$B_6H_6^{2-}$	a, c
	$B_7H_7^{2-}$	c
	$\cdot B_8H_8^-$	c
	$B_8H_8^{2-}$	c
	$B_9H_9^{2-}$	b
	$B_{10}H_{10}^{2-}$	a, b, d
	$B_{11}H_{11}^{2-}$	b
	$B_{12}H_{12}^{2-}$	a, b
Simple *nido*-borane ions	$B_5H_8^-$	e
	$B_6H_9^-$	a
	$\cdot B_8H_{12}^-$	e, f
	$B_9H_{12}^-$	e
	$B_9H_{14}^-$	g
	$B_{10}H_{12}^{2-}$	e
	$B_{10}H_{13}^-$	e, g
	$\cdot B_{10}H_{14}^-$	f
	$B_{10}H_{14}^{2-}$	e, f
	$B_{10}H_{15}^-$	e
	$B_{11}H_{13}^{2-}$	e
	$B_{11}H_{14}^-$	e
Linked *nido*-borane ions	$B_{18}H_{20}^{2-}$	e
	$B_{18}H_{21}^-$	e
	$B_{18}H_{22}^{2-}$	f
Linked *closo*-polyhedral ions	$B_{20}H_{18}^{2-}$	h
	$B_{20}H_{18}^{4-}$	h
	$B_{20}H_{19}^{3-}$	h
	$B_{24}H_{23}^-$	h

Early work on hydride ion formation has been reviewed.[897–9]

4. HYDRIDE ANIONS CONTAINING FRAMEWORK HETERO-ATOMS

In addition to borane anions with a purely boron-containing skeleton, a number of species are known which consist of a boron skeleton with one or more hetero-atoms.

(a) *Carbon*

There are a large number of anionic derivatives of carboranes which receive only cursory mention here (see, for example, M. F. Hawthorne, Accounts of Chemical Research, 1968, **1**, 281). These anions are, in general, prepared by degradation of a suitable carborane precursor, or by reaction of decaborane with isonitriles.

(b) *Nitrogen*

A few derivatives are known in which one nitrogen atom is incorporated into the boron framework. When decaborane(14) was treated with $Me_2N{-}N{=}S$, one of the products isolated was $(B_9H_{12}N.NMe_2)^-$.[82] This ion reacted with methyl iodide or excess sodium to yield respectively the inner salt $B_9H_{12}N,NMe_3$ or $B_9H_{12}NH$. It is likely that similar derivatives were obtained from the reaction of decaborane(14) with organic azides.[714–15]

(c) *Sulphur*

Decaborane(14) reacts essentially quantitatively with ammonium polysulphide in aqueous solution to give the $B_9H_{12}S^-$ ion, and pyrolysis of the cæsium salt yields $B_{10}H_{11}S^-$.[82] The latter species can also be obtained by treating decaborane(14) with $Bu^t–N=S=N–Bu^t$ or $Me_2N–N=S$.[82] The ion $B_{10}H_{10}S^{2-}$ is prepared by treating $B_{10}H_{11}S^-$ with a strong base, e.g. butyllithium.

B. Physical Properties of the Hydride Anions

The data on physical properties of the hydride anions are much more sparse than those on the hydrides. Application of topological and molecular orbital theories to the prediction of (a) the existence and (b) the electronic structures and spectra is discussed in Part 3.[22] It is of interest to note that a number of the hydride anions were theoretically predicted before they were found experimentally[214–15], and observed first electronic transitions have, in general, lent support to the theoretical calculations.

The measurements of polarizabilities and diamagnetic susceptibilities of a number of derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have been used to derive a Pascal constant for boron in these systems, and this in turn has been used to estimate magnetic susceptibilities of a number of closed-cage anionic species. The results are best interpreted in terms of a conducting sphere of boron atoms on which the cage electrons are relatively free to move under the influence of electric or magnetic fields.[900–1]

Undoubtedly, the most fully investigated physical properties of the hydride anions are their spectroscopic properties.

ELECTRONIC SPECTRA

The electronic spectra of the *closo*-polyhedral ions, in general, indicate the wide separation of the highest filled and lowest unfilled orbitals, in that only tail absorption is observed in the accessible u.v. region for most of the ions that have been examined. The only exception is that of $B_9H_9^{2-}$, which in the rubidium salt has λ_{max} 226 nm and ϵ_{max} 4040.[53] However, halogenation of the ions can lead to observation of electronic transitions, e.g. $B_8Br_6H_2^{2-}$ has two absorptions at λ_{max} 317 nm (ϵ 145) and 220 nm (ϵ 5000).[42] The units of absorbance, ϵ, are $l\ cm^{-1}\ mole^{-1}$.

The electronic spectra of the *nido*-borane anions were originally used for identification of species formed in reactions. Thus u.v. bands at 265 and 330 nm were assigned to the $B_{10}H_{13}^-$ ion produced in the aqueous hydroxide reaction with decaborane in dioxane solution.[902] Other bands in the system at 249 and 275 nm were assigned to $B_{10}H_{14}OH^-$ and $B_{10}H_{14},H_2O$. $Me_4NB_{10}H_{13}$ in acetonitrile showed bands at λ_{max} 267 (ϵ 2500) and 335 (ϵ 1730) nm.[475]

Benjamin et al. found the first stage of the OH^- attack on $B_{10}H_{14}$ gave $B_{10}H_{13}^-$, with u.v. maxima at 265 and 330 nm. A second product, $B_{10}H_{13}OH^{2-}$, had bands at 227 and 262 nm, while the final product $B_9H_{14}^-$ had $\lambda_{max}^{H_2O}$ 271 nm with ϵ_{max} 3980.[713] The dianion $B_{10}H_{12}^{2-}$ absorbs at 336 nm[903] and the u.v. absorption at λ_{max} 246 nm (ϵ 5400) has been used to characterize the $B_{10}H_{15}^-$ ion.[695,728] Pure $Et_3NHB_{11}H_{14}$ in CH_2Cl_2 cuts off in the u.v. at about 275 nm, whereas pure $CsB_{11}H_{14}$ in water is transparent, showing only a weak shoulder at 315 nm.[169]

The *n*- and *i*-ions from $B_{18}H_{22}$ have been studied in detail.[297] n-$B_{18}H_{20}^{2-}$ has bands at 350 (ϵ 7680) and 226 nm (ϵ 9260), while i-$B_{18}H_{20}^{2-}$ has bands at 335 (ϵ 4710), 289 (ϵ 5440), 264 (ϵ 6010) and 226 nm (ϵ 8604). The n-$B_{18}H_{21}^-$ showed absorptions at

375 (ϵ 4230), 330 (ϵ 3050), 256 (ϵ 2635) and 227 nm (ϵ 6440), while i-$B_{18}H_{21}^-$ had bands at 358 (ϵ 3630), 277 (ϵ 5460), 236 (ϵ 7110) and 226 nm (ϵ 7200).

The u.v. spectra of $B_{20}H_{18}^{2-}$ salts in water and acetonitrile solution were similar, showing strong absorption at 230–234 nm and a weak absorption at 290–293 nm.[182, 186] The u.v. spectrum of the double salt $(Et_3NH)_5B_{20}H_{18},B_{20}H_{19}$ showed maxima at 292 (ϵ $5{\cdot}5 \times 10^3$) and 223 nm (ϵ $1{\cdot}7 \times 10^4$).[187]

INFRA-RED SPECTRA

The infra-red spectra of nearly all the borane anions have been recorded, but the published details appear to be rather sparse.

Three principal absorptions of $B_6H_6^{2-}$ have been found at 2425, 1045 and 725 cm^{-1}, and these were consistent with octahedral symmetry.[33]

The instability of the $B_7H_7^{2-}$ ion has probably precluded the obtaining of its i.r. spectrum. The $B_8H_8^{2-}$ ion has shown bands at 2480, 2450, 1138, 1000, 950, 900, 860, 834, 715, 660, 630 and 620 cm^{-1} (nujol mull) and the B–H stretching modes in aqueous solution appear at 2455 and 2430 cm^{-1}.[42] The corresponding B–H vibrations of the $B_9H_9^{2-}$ ion in aqueous solution were observed at 2580, 2460, 2400 and 2350 cm^{-1}, while a nujol mull of the ion showed bands at 2540, 2478, 2445, 2415, 1050, 995, 960, 882, 760, 660 and 590 cm^{-1}.[53]

The $B_{10}H_{10}^{2-}$ ion has been studied by i.r. and Raman spectroscopy[56, 58], and although a definitive vibrational study has not been reported the spectrum of the triethylammonium salt has been described.[187] Similarly, the $B_{11}H_{11}^{2-}$ ion i.r. spectrum has been reported only from a pressed potassium bromide disc, with bands at 2450, 2360, 1060, 1020 and 720 cm^{-1}.[53] The $B_{12}H_{12}^{2-}$ ion has been the subject of a more rigorous vibrational investigation[58], its i.r. bands occurring at 2488, 1070 and 720 cm^{-1}, while the Raman spectrum (with depolarization ratios ρ in parentheses) showed shifts of 2518 (0·15), 2475 (0·77), 949 (0·85), 770, 743 (0·15) and 584 (0·85) cm^{-1}.

The *nido*-borane anions have generally been examined routinely by infra-red spectroscopy as a means of investigating the occurrence of bridging and terminal boron-hydrogen bonds. Inevitably the spectra are complex, and probably have not been completely resolved. The low symmetry of most of the ions makes any but the most obvious assignments of terminal B–H stretching modes extremely difficult. No infra-red data are available for $B_5H_8^-$ or $B_9H_{12}^-$, although bands have been reported for $B_{10}H_{12}^{2-}$ [735, 903], $B_{10}H_{13}^-$ [23, 903], $B_{10}H_{14}^{2-}$ [162], $B_{10}H_{15}^-$ [160], $B_{11}H_{13}^{2-}$ [169] and $B_{11}H_{14}^-$.[169] Some unpublished data[904] place the principal absorption of $B_9H_{14}^-$ at 2555 (m), 2462 (s), 2430 (sh), 2350 (sh), 1189 (m), 1165 (m), 1078 (w) and 1015 (m) cm^{-1}. Similar considerations apply to the linked polyhedral and fragment ions.

NUCLEAR MAGNETIC RESONANCE SPECTRA

Undoubtedly, the most important spectroscopic property of a borane anion is its ^{11}B n.m.r. spectrum.

The data on the n.m.r. spectra are presented in Table 7.2. A full discussion of these has been given in a recent monograph.[26]

THERMODYNAMIC PROPERTIES

The thermodynamic stability of aqueous $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions has been obtained by a study of the oxidation of $B_{10}H_{10}^{2-}$ to boric acid by aqueous permanganate using a calorimetric method.[908] ΔH_f° at 25° for $B_{10}H_{10}^{2-}$ is found to be $+22 \pm 5$ kcal mole^{-1}, and that of $B_{12}H_{12}^{2-}$ is estimated at $+11 \pm 10$ kcal mole^{-1}. The standard entropies ΔS° of these ions at 25°C are estimated as 60 ± 4 and 62 ± 4 e.u. for $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, and these data lead to standard free energies of formation ΔG_f° at 298K of 65 ± 5 and 63 ± 10 kcal mole^{-1}. It is therefore suggested that the apparent stabilities of these ions arise from kinetic rather than thermodynamic considerations.

Table 7.2.—N.m.r. Data of Borane Anions

(Chemical shifts are quoted relative to $B(OMe)_3$; values relative to BF_3,OEt_2 can be obtained by subtracting 18·2 ppm)

Ion	Position, if assigned	Chemical shift δ (ppm)	Relative intensity and multiplicity	Coupling constant *J* (Hz)	Operating frequency MHz	Reference
$B_6H_6^{2-}$	all	13	doublet	122	not stated	39
$B_7H_7^{2-}$		18·3	5 doublet	120	19·3	42
		40·7	2 doublet	119		
$B_8H_8^{2-}$	all	24·1	1 doublet	128	19·3	42
$B_9H_9^{2-}$		21·5	1 doublet	133	19·3	53
		39·6	2 doublet	124		
$B_{10}H_{10}^{2-}$	2, 3, 4, 5, 6, 7, 8, 9	47·2	8 doublet	128	not stated	20, 317
	1, 10	18·2	2	139		
$B_{11}H_{11}^{2-}$		35·0	10 doublet	125	19·3	53
		47·4	1 doublet	125		
$B_{12}H_{12}^{2-}$	all	34·3	doublet	124	20	681
$B_5H_8^-$	2, 3, 4, 5	35·2	4 doublet	127	19·3	106
	1	70·9	1 doublet	156		
$B_9H_{12}^-$	No details available.					645
$B_9H_{14}^-$	unassigned peaks	26·4	3 doublet	140	28·87*	146
		38·6	3 doublet ⎫ over-	132		
		41·9	3 doublet ⎭ lapping	140		
$B_{10}H_{12}^{2-}$	unassigned peaks	23·2	1 doublet	140	28·87	905
		25·7	4 broad singlet	—		
		40·9	2 broad doublet	~84		
		55·1	2 doublet ⎫ over-	140		
		60·0	1 doublet ⎭ lapping	140		
$B_{10}H_{13}^-$	unassigned peaks	60·0			12*	906, 907
		48·1				
		29·4				
		14·5				
$B_{10}H_{14}^{2-}$	1, 3		2 doublet	137	19·2*	162
	5, 7, 8, 10		4 doublet	132		
	6, 9		2 triplet	135		
	2, 4	highest field peak at +61·7 ppm	2 doublet	135		
$B_{10}H_{15}^-$	unassigned peaks	27·6			19·2	162
		34·9			12	160, 304, 728
		43·2				
$B_{11}H_{13}^{2-}$		38·4	doublet	125		53
		49·6	doublet	125		
$B_{11}H_{14}^-$		34·2	doublet	140	19·2	169
n-$B_{18}H_{20}^{2-}$	unassigned peaks	42·7			19·3*	297
		36·2				
		27·5				
		18·8				
		10·9				
		0·5				
		−6·7				
i-$B_{18}H_{20}^{2-}$	unassigned peaks	46·2			19·3*	297
		38·9				
		16·6				
		10·4				
		5·2				
		−3·0				
		−34·7				

* Denotes that a plot of the spectrum has been published.

Refs. p. 332

Table 7.2.—cont'd.

Ion	Position, if assigned	Chemical shift δ (ppm)	Relative intensity and multiplicity	Coupling constant J (Hz)	Operating frequency MHz	Reference
n-$B_{18}H_{21}^{-}$		44·6			19·3*	297
	unassigned peaks	35·2				
		29·4				
		19·5				
		14·5				
		7·5				
		0·0				
		−8·3				
		−15·3				
i-$B_{18}H_{21}^{-}$		46·7			19·3*	297
	unassigned peaks	39·5				
		27·1				
		15·9				
		13·6				
		7·5				
		−1·4				
		−7·2				
		−27·5				
n-$B_{18}H_{22}^{2-}$	Not reported.					
i-$B_{18}H_{22}^{2-}$	Not reported.					
$B_{20}H_{18}^{2-}$	not definitely assigned	44·3	2 doublet		60*	182
		38·3	overlapping			
		34·9	12 doublets			
		31·6				
		25·8	2 doublet			
	6, 6′,	2·9	2 singlet			
		−11·7	2 doublet			
$B_{20}H_{18}^{4-}$ aa isomer	all positions except	46·0	16 doublet	115	32·1*	187
	1, 1′	23·4	2 doublet	130		
	10, 10′	7·1	2 broad singlet			
$B_{20}H_{18}^{4-}$ ae isomer		46·9	16 ‘doublet’	‘102’	32·1*	187
		23·7	doublet			
	1, 10, 1′	19·3	3 doublet			
		14·5	doublet			
	10′	7·2	1 singlet			
$B_{20}H_{18}^{4-}$ ee isomer	all positions except	46·2	16 broad		32·1*	187
	1, 1′ and	20·9	2 doublet	130		
	10, 10′	16·1	2 doublet	130		
$B_{20}H_{19}^{3-}$ (stable isomer, probably ae)	all positions except	46·1	16 doublet		32·1*	187
		41·9	doublet			
	1, 1′, 10, 10′	19·2	4 ‘doublet’	150		
		~24·2	‘doublet’			

* Denotes that a plot of the spectrum has been published.

PART 8: HYDRIDIC REPLACEMENT IN THE BORANE ANIONS

A general feature of the chemistry of derivatives of the boron hydrides is that in a large number of species the hydride ion H^- may be considered as a ligand replaceable by another two-electron donor species. This can be another anionic species, e.g. OH^-, CN^-, Cl^- or, more importantly, it may be a neutral species such as RCN, R_3N, R_2S, R_3P, CO, etc.

Of the simple *nido*-species, derivatives of neutral ligands of a large number of known or hypothetical ions have been characterized, whereas for the *closo*-polyhedral ions and linked *nido*- and *closo*-polyhedral ions fewer derivatives have been characterized to date. A summary of these for the higher boranes is presented in Table 8.1.

Table 8.1.—Ligand Derivatives of Borane Anions

Anion	$B_4H_{10}^{2-}$	$B_5H_{11}^{2-}$	$B_8H_{13}^{-}$	$B_9H_{14}^{-}$
Derivative	$B_4H_8L_2$	$B_5H_9L_2$	$B_8H_{12}L$	$B_9H_{13}L$
Reference	764	764	132, 133, 136	645, 713, 904, 909
Anion	$B_{10}H_{13}^{-}$	$B_{10}H_{14}^{2-}$	$B_{10}H_{14}^{2-}$	$B_{10}H_{10}^{2-}$
Derivative	$B_{10}H_{12}L$	$B_{10}H_{13}L^-$	$B_{10}H_{12}L_2$	$B_{10}H_9L^-$
Reference	907	878, 907, 907a	877, 907, 910, 911	912, 913, 914
Anion	$B_{10}H_{10}^{2-}$	$B_{12}H_{12}^{2-}$	$B_{12}H_{12}^{2-}$	$B_{20}H_{18}^{2-}$
Derivative	$B_{10}H_8L_2$	$B_{12}H_{11}L^-$	$B_{12}H_{10}L_2$	$B_{20}H_{16}L_2$
Reference	913, 914, 915, 916	917, 918	913, 915	186

A. Derivatives of the Type $B_{10}H_{12}L_2$

Undoubtedly, the bulk of the work carried out on compounds of this type has concerned the derivatives $B_{10}H_{12}L_2$, and the original characterization of species of this type was carried out in 1957 by Schaeffer, who isolated $B_{10}H_{12}(MeCN)_2$ from the reaction of acetonitrile with decaborane(14)[910]:

$$B_{10}H_{14} + 2MeCN \rightarrow B_{10}H_{12}(MeCN)_2 + H_2$$

Subsequently, a large number of similar derivatives were characterized, utilizing nitriles, dialkyl cyanamides, phosphines and other Group V donors such as phosphite, phosphinites, arsines, etc., amides, amines, thioureas, tetrazoles, sulphides, sulphoxides, phosphine oxides and other ligands. (See references 467, 476, 779–84, 787, 865, 877, 907, 911, 919–56.)

Bidentate ligands L* such as $(Me_2NCH_2)_2$, $(Et_2NCH_2)_2$ and $(Ph_2PCH_2)_2$ have also been used to prepare compounds of formula $L^*B_{10}H_{12}$.[911, 938, 941, 944, 946, 950]

LIGAND REPLACEMENT REACTIONS OF $B_{10}H_{12}L_2$

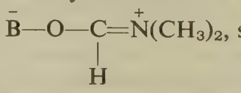
A useful synthetic route to a variety of the $B_{10}H_{12}L_2$ compounds, which can in general be applied also to the other derivatives of neutral ligands, involves replacement of one ligand by another. Thus, reactions of the type:

$$B_{10}H_{12}L_2 + 2L' \rightarrow B_{10}H_{12}L'_2 + 2L$$

occur where a weakly-bonded ligand is replaced by one which bonds more strongly. Studies of displacement reactions[877, 919, 929] have yielded the partial displacement series:

$$Me_2S < MeCN < Et_2NCN < Et_3As < HCONMe_2$$
$$= CH_3CONMe_2 < (EtO)_3P < C_5H_5N \simeq Et_3N \simeq Ph_3P \leqslant \text{amidine}$$

The structure of the $B_{10}H_{12}L_2$ compounds has been established from *X*-ray studies of $B_{10}H_{12}(MeCN)_2$[163–4], $B_{10}H_{12}(Me_2S)_2$[957] and $B_{10}H_{12}(2\text{-}BrC_5H_4N)_2$.[165–7]

A complete assignment of the ^{11}B n.m.r. spectra of a series of the compounds has been made[326], and the mode of attachment of dimethylformamide in $B_{10}H_{12}(DMF)_2$ was deduced to be oxygen-bonded of the type  $\overset{-}{B}{-}O{-}\underset{\underset{H}{|}}{C}{=}\overset{+}{N}(CH_3)_2$, since there was a relatively large barrier to rotation about the C–NMe₂ bond.[958] The bonding in the $B_{10}H_{12}L_2$ compounds has been the subject of some conjecture. It is observed that the stabilities of the complexes do not follow the simple sequence of base strength of the ligands. Furthermore, a number of the complexes, e.g. those derived from pyridines, are unusual in that they are highly coloured, and this has been suggested to arise from charge-transfer.[933] Similar reasoning has been used to describe the stability of complexes in terms of good *n*-donor and *π*-acceptor properties of the ligands.[959, 960]

In this context, it is relevant that a study of the effect of solvent polarity on the long wave-length absorption band of $B_{10}H_{13}py^-$ led to a satisfactory correlation of transition energy with the solvent parameter Z (as described by Kosower[961]), yielding the expression $Z = 0{\cdot}556\ E_T + 21{\cdot}8$ which was interpreted as further evidence of the intramolecular charge-transfer nature of the visible absorption band.[962–3]

The ultra-violet absorption spectrum of a series of $B_{10}H_{12}L_2$ complexes has been studied and correlated with their relative stability.[911] The u.v. spectra are due to π to π^*, or π to non-bonding transitions between molecular orbitals involving the 5,6,7- (and 8,9,10-) boron atoms and the ligand donor atom. The ligand modifies the orbital energies and hence the position of the u.v. absorption band depends on the donor power of the ligand. Where the ligand has a vacant orbital of π symmetry with respect to B(6) (which has p_π symmetry), there is also the possibility of back donation; hence phosphines are stronger donors than sulphides, which in turn are stronger donors than ethers. It is important to stress, however, that one can validly compare the u.v. spectra only of compounds having the same donor atom. The phosphine ligands were placed in the following sequence of donor strengths (ν_{max}, cm^{-1}, in parentheses below each ligand):

$$\underset{\text{(near cut-out peak for MeCN)}}{Ph_3P \simeq Ph_2PH \simeq PhPH_2} > \underset{(41{,}000)}{(Me_2N)_3P} > \underset{(40{,}000)}{(MeO)_3P} >$$

$$\underset{(38{,}900)}{PhP(NMe_2)_2} > \underset{(38{,}600)}{(PhO)_3P} > \underset{(37{,}500)}{(Me_2N)_2PCl} > \underset{(36{,}800)}{PhP(Cl)NMe_2}$$

Likewise, the sulphide ligand strength in $L_2B_{10}H_{12}$ complexes decreases in the sequence:

$$\underset{(42{,}700)}{C_4H_8S} > \underset{(41{,}300)}{Et_2S} > \underset{(41{,}000)}{Me_2S} > \underset{(39{,}200)}{C_4H_8OS}$$

Complexes with *sym*-diphenylthiourea, dimethyl sulphoxide, methyl cyanide and phenyl cyanide were also studied.

A study of[963–4] the kinetics of the ligand exchange reaction which produces $B_{10}H_{12}(Et_3N)py$ from pyridine and $B_{10}H_{12}(Et_3N)_2$ yielded results which were interpreted in terms of an intermediate $B_{10}H_{12}(Et_3N)$ common to this and the competing reaction which produces $B_{10}H_{10}^{2-}$. The mechanism consistent with the results was:

$$B_{10}H_{12}(Et_3N)_2 \rightleftharpoons B_{10}H_{12}(Et_3N) + Et_3N$$

$$\left.\begin{array}{r} B_{10}H_{12}(Et_3N) + Et_3N \rightarrow \\ B_{10}H_{12}(Et_3N) + py \rightarrow \end{array}\right\} \text{ionic products} \xrightarrow{\text{fast}} B_{10}H_{10}^{2-}$$

$$B_{10}H_{12}(Et_3N) + py \rightarrow B_{10}H_{12}(Et_3N)py$$

It has been suggested that the intermediate $B_{10}H_{12}(Et_3N)$ is different in nature from the known derivative of $B_{10}H_{13}^-$, $B_{10}H_{12}(SMe_2)$.[907] This suggestion is in agreement with the scheme:

$$B_{10}H_{12}(SMe_2)_2 \rightleftharpoons \underset{\text{reactive species}}{B_{10}H_{12}(SMe_2)} + SMe_2$$

$$\underset{\text{reactive species}}{B_{10}H_{12}(SMe_2)} \rightleftharpoons \underset{\text{stable species}}{B_{10}H_{12}(SMe_2)}$$

The reactions of substituted decaboranes with ligands have been reported to yield substituted $B_{10}H_{12}L_2$ derivatives.[927, 941, 944, 950–1, 965] Thus, $2\text{-}BrB_{10}H_{13}$ on treatment with Et_2S, MeCN or Ph_3P yielded respectively the appropriate $B_{10}H_{11}BrL_2$ derivative, and mixed 1- and $2\text{-}EtB_{10}H_{13}$ behaved similarly. Ligand-exchange reactions were observed to take place with both the bromine- and ethyl-substituted derivatives.

Reactions involving the tertiary amines Me_3N and Et_3N with the substituted decaborane(14) or substituted bis(diethylsulphide)decaborane(12) in general yielded equatorially substituted $B_{10}H_9X^{2-}$ derivatives.

In contrast with a number of other donors, alkyl isocyanides do not react with decaborane(14) to produce $B_{10}H_{12}L_2$ derivatives, but rather to insert a carbon atom into the boron skeleton with formation of a formal derivative of the $B_{10}CH_{13}^-$ ion, e.g. with EtNC, decaborane yields $EtNH_2,B_{10}CH_{12}$.[966]

FURTHER REACTIONS OF $B_{10}H_{12}L_2$ COMPOUNDS

Derivatives of the type $B_{10}H_{12}L_2$ or $B_{10}H_{13}L^-$ have been shown to undergo skeletal degradation by alcoholysis or controlled hydrolysis to yield initially formal derivatives of $B_9H_{14}^-$. Thus $B_{10}H_{12}(MeCN)_2$ on treatment with ROH yields $B_9H_{13}.NH{=}C(Me)OR$[645, 910, 967], and $B_{10}H_{12}(Et_2S)_2$ reacts rapidly with methanol to form $B_9H_{13}Et_2S$.[645, 718, 967–8] Acid hydrolysis of $B_{10}H_{13}L^-$ ions also yielded $B_9H_{13}L$ derivatives[645, 878], and further degradation occurred under appropriate conditions.[718, 860]

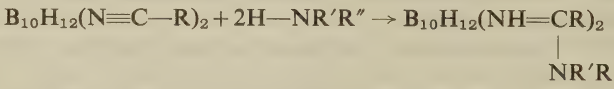
A reaction involving substitution of the boron skeleton has been described[969, 970]:

$$B_{10}H_{12}(SR_2)_2 + HX \xrightarrow[\text{Benzene}]{20°} 6\text{-}(5\text{-})XB_{10}H_{13} + 2SR_2$$

where X = F, Cl, Br or I. The structures of the derivatives were established by i.r. and ^{11}B n.m.r. spectra.[971]

Furthermore, $(Me_2S)_2B_{10}H_{12}$ reacts with sulphuric acid in benzene to yield 6,6′-oxidobistridecahydrodecaborane $B_{20}H_{26}O$, and small quantities of $B_{10}H_{14}O_2$. The $B_{20}H_{26}O$ further reacts with dimethyl sulphide to give $(Me_2S)_2B_{10}H_{12}$ and $Me_2SB_9H_{13}$, or with tetrahydrofuran to produce THF,B_9H_{13}.[972]

Reactions involving the ligands rather than the boron framework have also been reported. Thus, nucleophilic substitution has been shown to occur at phosphorus in bis(chlorodiphenylphosphine)decaborane[925, 943, 949, 954]; bis)azodiarylphosphine)decaborane[942], and bis(acetonitrile)decaborane will add a variety of protonic amine or hydrazine compounds across the C≡N bond[24, 865, 878, 925, 973]:



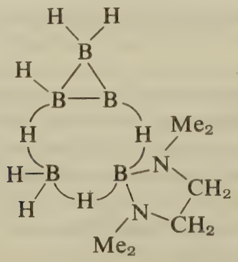
$$B_{10}H_{12}(N{\equiv}C{-}R)_2 + 2H{-}NR'R'' \rightarrow B_{10}H_{12}(NH{=}\underset{\displaystyle NR'R''}{\underset{|}{C}}R)_2$$

Thus reactions occur with primary or secondary amines, hydrazine and methylhydrazine, 5-aminotetrazole and nitroguanidine. With hydrazine or aqueous methanolic sodium hydroxide the reaction has been reported to proceed further to give bis(ammonia)decaborane(12).

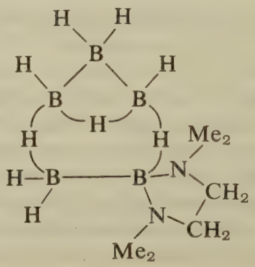
Decaborane–phosphine polymers have been prepared by suitable polymerization of $B_{10}H_{12}(Ph_2PCl)_2$ and $B_{10}H_{12}(Ph_2POH)_2$. Furthermore $B_{10}H_{12}(Ph_2PN_3)_2$ yields stable polymers on treatment with diphosphines.[943, 948, 953–4, 974]

B. Formal Derivatives of other Small *nido*-Anions

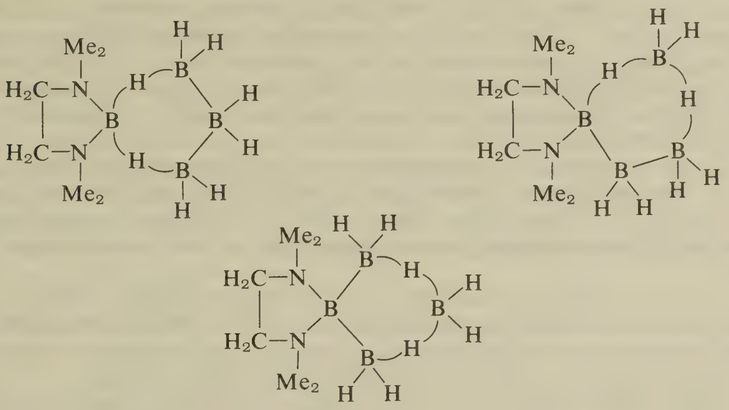
Derivatives of the hypothetical anions $B_5H_{11}^{2-}$ and $B_4H_{10}^{2-}$ have been prepared by treating pentaborane(9) with N,N,N′,N′-tetramethylethylenediamine, which forms the colourless crystalline B_5H_9,TMED.[764] On the basis of n.m.r. data, the structure was suggested to be either



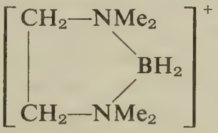
or



When B_5H_9,TMED was treated with methanol, a second product B_4H_8,TMED was obtained, for which one of the following three structures was favoured:



Both compounds gave the cation



in nearly quantitative yield on acid hydrolysis.

A derivative of the hypothetical $B_8H_{13}^-$ ion, first thought to be a $B_9H_{14}^{2-}$ derivative, $EtNH_3^+B_9H_{12}NH_2Et^-$ [645], but later shown to be $EtNH_2B_8H_{11}NHEt$[136–8], was prepared by an attempted ligand displacement reaction of ethylamine on $B_9H_{13}SEt_2$. A number of derivatives of the type $B_8H_{12}L$ have been prepared from B_8H_{12} and ligand[132–3] (see Part 6). A number of derivatives of $B_9H_{14}^-$ have already been discussed as reaction products of hydrolytic or alcoholic degradation of $B_{10}H_{13}L^-$ and $B_{10}H_{12}L_2$ species. In addition, derivatives may also be prepared directly from the $B_9H_{14}^-$ ion[713]:

$$Me_3NH^+B_9H_{14}^- \xrightarrow{\text{heat}} Me_3NB_9H_{13} + H_2$$
$$Me_4N^+B_9H_{14}^- + HCl + MeCN \longrightarrow MeCNB_9H_{13} + Me_4NCl + H_2$$

The $B_9H_{13}L$ derivatives in general undergo ligand displacement reactions in an analogous manner to the $B_{10}H_{12}L_2$ species.[645] Thus derivatives of acetonitrile, triethylamine, triphenylphosphine and substituted pyridines have been prepared from $B_9H_{13}SEt_2$, and the pyridine derivatives were observed to be highly coloured. Furthermore, $B_9H_{12}L^-$ ions were obtained by treating the $B_9H_{13}L$ species with sodium hydride, although when $B_9H_{13}SEt_2$ was treated with strong bases such as Ph_3PCH_2 or Me_4NOH, proton abstraction and ligand expulsion were observed with the formation of $B_9H_{12}^-$. In addition, $B_9H_{13}L$ could be regenerated by treating $B_9H_{12}^-$ with pyridinium chloride.

Another convenient general preparation of $B_9H_{13}L$ is the electrochemical oxidation of $B_9H_{14}^-$ in presence of the appropriate ligand.[904] By a combination of electrochemical oxidation and ligand replacement reactions, numerous $B_9H_{13}L$ complexes were prepared (e.g. L = T.H.F., Me_2S, Et_2S, MeCN, Et_3N, Et_2NH, py, α-pic, Bu_3P, Ph_3P, and Ph_2PH).[904]

A number of salts of the $B_{10}H_{13}L^-$ anions have been prepared by treating $B_{10}H_{13}^-$ with ligand. The $B_{10}H_{13}L^-$ ions could be treated with amine-hydrochlorides to yield unsymmetrical $B_{10}H_{12}LL'$, and potentiometric titration with hydrogen chloride in dioxan indicated that a derivative of $B_{10}H_{15}^-$, namely $B_{10}H_{14}L$, was formed, although the compound was not isolated.[878]

C. Derivatives of the *closo*-Polyhedral Ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$

SPECIES OF THE TYPE $B_{10}H_9L^-$, $B_{10}H_8L_2$, $B_{12}H_{11}L^-$ AND $B_{12}H_{10}L_2$

It is relevant to note first the possibility of isomeric compounds in substituted polyhedral species.[975] Thus $B_{12}H_{12}^{2-}$ is a symmetric species with all boron positions equivalent (Part 2). It can be visualized as a sphere with two 'tropical' belts (Fig. 8.1), and mono-substitution results in the definition of a 'polar' B_1. A second substituent may then be inserted in one of three positions, namely (a) in the first 'tropical' belt, all five positions of which are equivalent (i.e. 1,2-disubstitution), (b) in the second 'tropical' belt (i.e. 1,7-substitution) or (c) at the other pole (i.e. 1,12-substitution). The numbers of isomers from tri-substitution will be correspondingly greater, i.e. 1,2,3-; 1,2,4-; 1,2,7-; 1,2,8-; 1,2,9-; 1,2,12-; some of these have non-superimposable mirror images and are therefore potentially resolvable into optical isomers.

In $B_{10}H_{10}^{2-}$ the apical and equatorial positions are intrinsically different, and the species may be considered as an ellipsoid (Fig. 8.2). There will therefore be two isomeric mono-substituted derivatives, 1-, and 2-, and a greater number of di-substituted derivatives, i.e. 1,2-; 1,6-; 1,10-; 2,3-; 2,4-; 2,6- and 2,7-.

Derivatives of the type $B_{12}H_{11}L^-$ and $B_{12}H_{10}L_2$ were first isolated as by-products of preparations of $B_{12}H_{12}^{2-}$ by B–H condensation reactions[25, 679, 681], but the isomer constitution of the di-substituted derivatives was not established. Subsequently, the conditions for the preparation of the carbonyl derivatives $B_{12}H_{10}(CO)_2$ and $B_{12}H_{11}CO^-$ from the reaction of carbon monoxide with acidic $B_{12}H_{12}^{2-}$ could be adjusted to give yields of 1,7- and 1,12- isomers.[915, 918, 976] These then serve as starting materials for other $B_{12}H_{10}L_2$ and $B_{12}H_{11}L^-$ derivatives. The reaction with carbon monoxide proceeds through the initial formation of $B_{12}H_{11}COOH^{2-}$ and $B_{12}H_{10}(COOH)_2^{2-}$, which yield the carbonyl derivatives on dehydration. Similarly, a

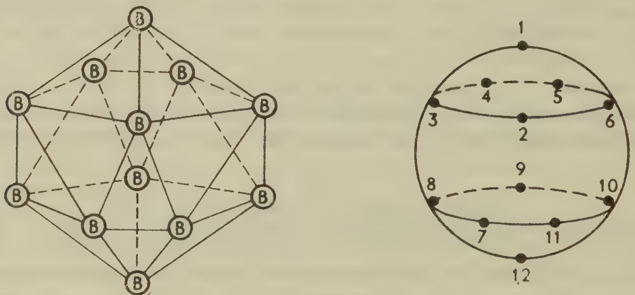


FIG. 8.1

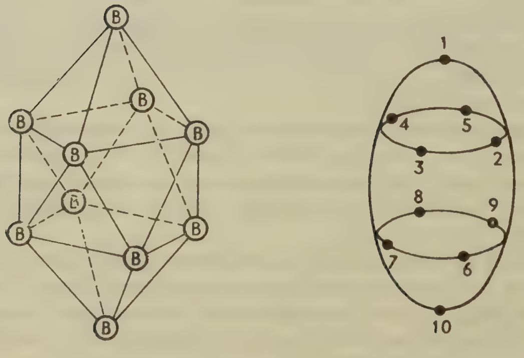


FIG. 8.2

range of derivatives of the type $B_{12}H_{10}L_2$ and $B_{12}H_{11}L^-$ could be obtained by treating $B_{12}H_{12}^{2-}$ with bases such as sulphones, sulphonamides, tetramethylurea, nitriles, nitrobenzene, and N-methylpyrrolidone, using strongly acid media.[917, 977]

Another route to the $B_{12}H_{10}L_2$ and $B_{12}H_{11}L^-$ derivatives involves treating the $B_{12}H_{12}^{2-}$ ion with aqueous hydroxylamine-O-sulphonic acid. By this method all three possible isomers of $B_{12}H_{10}(NH_3)_2$ are formed and may be separated by virtue of their respective solubilities in water and acetonitrile.[913] Subsequent treatment with dimethyl sulphate in basic solution yields the corresponding $B_{12}H_{10}(NMe_3)_2$ isomers.

Similar, and perhaps more extensive, work has been carried out on the preparation and properties of the corresponding derivatives of $B_{10}H_{10}^{2-}$, namely $B_{10}H_8L_2$ and $B_{10}H_9L^-$. Diazonium derivatives of $B_{10}H_{10}^{2-}$ have been prepared by treating $B_{10}H_{10}^{2-}$ with a large excess of nitrous acid, followed by reduction, preferably with alcoholic sodium tetrahydroborate[915, 978–81]:

$$(NH_4)_2B_{10}H_{10} + \overset{\text{(excess)}}{HONO} \longrightarrow \text{Explosive intermediate} \xrightarrow{NaBH_4} B_{10}H_8(N_2)_2$$

$B_{10}H_8(N_2)_2$ serves as a useful intermediate for the preparation of a wide range of derivatives of the type $B_{10}H_8L_2$, since the nitrogen ligand is easily displaced by a variety of weak and strong nucleophiles, e.g. ammonia[978, 982], amines[978, 983], hydrogen sulphide[978], azide ion[978], hydroxide ion[978], nitriles[978], and carbon monoxide.[978–80]

Similar reactions occur with nitrous acid and derivatives of $B_{10}H_{10}^{2-}$, to produce species such as $B_{10}Cl_8(N_2)_2$[978], $B_{10}I_8(N_2)_2$[860], $B_{10}H_8(N_2)NMe_3$[982], $B_{10}H_8(N_2)SMe_2$[914], and $Me_2SB_{10}H_7(NH_3)(N_2)^+$.[983]

Carbonyl derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ may also be prepared by treating suitable salts with oxalyl chloride.[916, 983] Thus reaction of oxalyl chloride with 1-$B_{10}H_9SMe_2^-$, 2-$B_{10}H_9NMe_3^-$ and $B_{12}H_{11}NMe_3^-$ gave respectively 1,6-$Me_2SB_{10}H_8CO$, 2,4- and 2,7(8)-$Me_3NB_{10}H_8CO$ and $Me_3NB_{12}H_{10}CO$.

The carbonyl group in these compounds was found to react with a variety of reagents leading to a large number of derivatives. Thus the carbonyl group is readily converted to amine, isocyanate[915, 918], nitrile[915, 918], alkyl, hydroxymethyl[984], carboxyl[915, 918], acyl[918], and ketonic derivatives.[985]

Furthermore, resolution of optically active derivatives, e.g. of the 2,7(8)- isomer of $Me_3NB_{10}H_8CO$, has been carried out by converting it to $H_3O^+Me_3NB_{10}H_8COOH^-$ and fractionally crystallizing the brucine salt.[916, 983]

Other derivatives of the type $B_{10}H_8L_2$ and $B_{10}H_9L^-$ have been prepared from $B_{10}H_{10}^{2-}$ by amination with hydroxylamine-O-sulphonic acid[913], reaction with dimethylsulphoxide and hydrochloric acid[914], reaction with dimethylformamide under acid conditions[977], reaction with Lewis bases under acid conditions[917], direct reaction with carbon monoxide under acid conditions[918] and reactions with electrophilic reagents such as Vilsmeier reagent, $CHCl{=}NMe_2^+Cl^-$.[986]

In contrast with the facile ligand exchange processes which occur in the $B_{10}H_{12}L_2$ series of compounds, and with $B_{10}H_{12}(SMe_2)_2$ in particular, there are few well characterized ligand replacement reactions reported for derivatives in the series $B_{10}H_8L_2$. For instance, $B_{10}H_8(SMe_2)_2$ reacts with tributylphosphine or potassium phthalimide by demethylation to form $Me_2SB_{10}H_8SMe$ and there is no evidence for displacement of the SMe_2 ligands.[914]

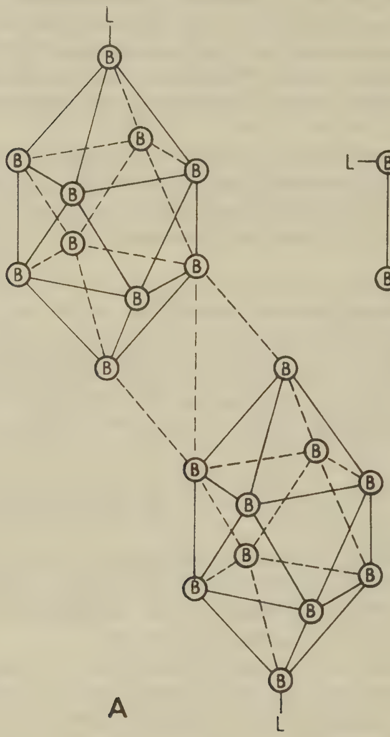
LINKED POLYHEDRAL SPECIES

A number of derivatives of $B_{20}H_{18}^{2-}$ have been obtained by cerium(IV) ion oxidation of derivatives of the type $B_{10}H_9L^-$.[186]

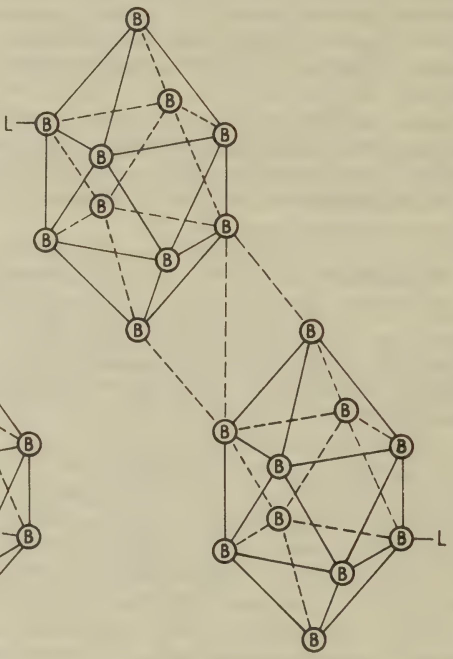
$$2B_{10}H_9L^- \rightarrow B_{20}H_{16}L_2 + 2H^+ + 4e^-$$

Ligands on the $B_{10}H_9L^-$ species which have yielded coupled structures include SMe_2, IC_6H_5, $O{=}\underbrace{C{-}(CH_2)_3N}Me$, and $(CH_2)_4SO_2$. Since the original ions $B_{10}H_9SMe_2^-$ and $B_{10}H_9IC_6H_5^-$ had ligands in apical sites, and $B_{10}H_9O\underbrace{C(CH_2)_3N}Me^-$ and

$B_{10}H_9O_2S(CH_2)_4^-$ had ligands in equatorial sites, it was assumed that no displacement or rearrangement of ligands occurred during the oxidation and therefore that the structures of the ions were respectively (A) and (B):



A



B

Geometrical isomers of derivatives of $B_{20}H_{18}^{2-}$ have also been obtained by reaction of bases with $B_{20}H_{16}$.[89] Thus, species $B_{20}H_{16}L_2$ have been prepared with the ligands SMe_2[89], PEt_3[89], NMe_3[89], OEt_2[89], and MeCN.[90] The structure of the adduct

$$B_{20}H_{16}(MeCN)_2,MeCN$$

is discussed in Part 2.[92]

PART 9: FURTHER CHEMICAL PROPERTIES OF THE HYDRIDE ANIONS

A. *Closo*-Polyhedral Species

(i) SIMPLE SUBSTITUTION

In principle any hydrogen in a *closo*-polyhedral borane anion should be replaceable by other groups such as halogen, pseudohalogen, -OR, -R, etc. Indeed, a large number of halogenated species of the anions and their derivatives are known, and most of them have been prepared by direct reaction of the anion with halogen or simple halogenating agent. Thus, in the smaller polyhedral ions, the brominated derivatives $B_6Br_6^{2-}$, $B_8Br_6H_2^{2-}$ and $B_9Br_6H_3^{2-}$ have been prepared by treating $B_6H_6^{2-}$, $B_8H_8^{2-}$ or $B_9H_9^{2-}$ with sodium hypobromite.[42,53] The B_6 and B_8 species are acid-stable, whereas $B_9Br_6H_3^{2-}$ is degraded by acid. The chlorinated derivative $B_9Cl_8H^{2-}$, prepared by treating B_9Cl_8H with water[55], is also unstable in acid solution. $B_{11}H_{11}^{2-}$ reacts with sodium hypobromite to yield $B_{11}Br_9H_2^{2-}$ whereas reaction with bromine or N-chlorosuccinimide cleaved a framework boron atom, to give respectively $B_{10}Br_{10}^{2-}$ and $B_{10}Cl_8H_2^{2-}$.

Refs. p. 332

The simple substitution chemistry of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ is much more extensive than that of the lower homologues. No exchange occurs between deuterium oxide and $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ at pH values above about 4, although at lower pH values complete exchange yields $B_{10}D_{10}^{2-}$ or $B_{12}D_{12}^{2-}$.[57] Rates of exchange are dependent on position, the apical (1,10) sites on $B_{10}H_{10}^{2-}$ being the most easily replaced.

Halogenated derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have been prepared by a variety of routes. Thus 2-$BrB_{10}H_{9}^{2-}$ was isolated from the reaction of 2-$BrB_{10}H_{13}$ with basic reagents.[927] This method is of use when specifically substituted products are required. In general, preparations of halogen derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are best carried out by direct halogenation of the parent ions. Thus the species $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ react smoothly in aqueous or alcoholic solutions[912, 987] with chlorine, bromine, iodine, N-iodosuccinimide and similar reagents to give derivatives in which from one to all the hydrogens have been replaced by halogens. Halogenation has also been accomplished with hydrogen halides or even elemental fluorine[987], although the latter causes degradation of $B_{10}H_{10}^{2-}$ and yields $B_{12}F_{11}OH^{2-}$ from $B_{12}H_{12}^{2-}$.

All of the halogens react rapidly in the initial stages. In iodine substitution of $B_{10}H_{10}^{2-}$ at −40°, the first three iodine atoms to enter are kinetically indistinguishable, whereas it was possible to stop the iodination of $B_{12}H_{12}^{2-}$ at $B_{12}H_{11}I^{2-}$, and further iodination resulted in a 5:1 ratio of 1,7- to 1,2-$I_2B_{12}H_{10}$ with only a trace of the 1,12-isomer. Bromination of $B_{10}H_{10}^{2-}$ at 0° proceeded readily to the $B_{10}H_3Br_7^{2-}$ stage, and in refluxing ethanol went to completion in forming $B_{10}Br_{10}^{2-}$, whereas the $B_{12}H_{12}^{2-}$ ion yielded $B_{12}H_6Br_6^{2-}$ and $B_{12}H_2Br_{10}^{2-}$ under comparable conditions. More forcing reaction conditions were needed to brominate $B_{12}H_{12}^{2-}$ completely to $B_{12}Br_{12}^{2-}$.[987] Chlorination of $B_{10}H_{10}^{2-}$ at 0–5° yielded $B_{10}H_2Cl_8^{2-}$ although at ambient temperature complete chlorination was achieved, whereas with $B_{12}H_{12}^{2-}$ comparable chlorination conditions yielded $B_{12}H_6Cl_6^{2-}$ and products approximating to $B_{12}H_{2\cdot5}Cl_{9\cdot5}^{2-}$, and elevated temperatures were necessary for complete chlorination. These studies suggest that the order of reactivities is $B_{10}H_{10}^{2-} > B_{12}H_{12}^{2-}$, and $F(?) > Cl > Br > I$.

The halogenated derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ have excellent thermal and oxidative stabilities as salts of electro-positive cations, but although the conjugate acids of these anions are very strong acids they are not as thermally stable as the salts. Thus $Cs_2B_{10}Cl_{10}$ is not oxidized at a half-wave potential ($E_p/_2$) of +1·1 V (standard calomel electrode); with $Cs_2B_{10}H_2Cl_8$ and $Cs_2B_{10}Br_{10}$ oxidation begins near $E_{p/2}$ +1·1 V, and $Cs_2B_{10}I_{10}$ is oxidized at $E_{p/2}$ +1·3 V. No reduction at a dropping mercury electrode with potentials +0·3 to −1·9 V was observed.[987] The lower thermal stability of the acids of the anions is exemplified by that of $B_{10}Cl_{10}^{2-}$; the hydrated acid decomposes at 260° yielding red crystals of B_9Cl_8H and other volatile and non-volatile products of decomposition.[55] The structure of B_9Cl_8H was not established, although it was thought probably not to be a tricapped trigonal prism as in $B_9H_9^{2-}$ but possibly a square-capped square antiprism. B_9Cl_8H reacted with water to yield $B_9Cl_8H^{2-}$.

Simple substitution of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ has also been described for a wide variety of substituents, e.g. —OH, —OR, —SH, —SR, $—\overset{\overset{\displaystyle O}{\|}}{C}—R$, $—O—\overset{\overset{\displaystyle O}{\|}}{C}—R$ or —R[912, 977], —CN, —N_3, $—\overset{\overset{\displaystyle O}{\|}}{C}NH_2$, —N=C=O, $—\overset{\overset{\displaystyle O}{\|}}{C}—OR$[801], —$NH_2$[978] and —N=N—Ar.[988–9]

Thus, acidic $B_{10}H_{10}^{2-}$ reacts with benzoyl chloride in dimethoxyethane to give $B_{10}H_9COC_6H_5^{2-}$, which is dark red and protonated in acid solution, from which acid salts may be precipitated, although in basic solution it is light yellow and can be precipitated as neutral salts.[977] The $B_{10}H_9COC_6H_5^{2-}$ group behaves like an organic ketone in that its semicarbazone is readily prepared, and it is reported to be oxidized by hydrogen peroxide to $B_{10}H_9OCOC_6H_5^{2-}$ which may subsequently be hydrolyzed to $B_{10}H_9OH^{2-}$, although other work on $B_{10}H_9OH^{2-}$ showed it, in fact, to be $B_{20}H_{17}OH^{4-}$ (see below). $B_{12}H_{12}^{2-}$ reacts with benzoyl chloride to yield boron–

oxygen bonded species which may be brominated to $B_{12}Br_{10}(OH)_2^{2-}$; reaction with benzoyl *p*-toluene sulphonate gives $B_{12}H_{11}OCH_2C_6H_5^{2-}$. A patent has appeared for the preparation of $H_2B_{12}H_{12}$ from $B_{12}H_{12}^{2-}$ and strong acid.[990]

Under acid conditions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ react with ethers to give alkoxy-substituted products, although mixtures of anions of varying degrees of substitution can be obtained. Acids, alcohols, formaldehyde and ketones all react with $B_{12}H_{12}^{2-}$ under acid conditions to give boron–oxygen bonded derivatives which are often mixtures which are difficult to separate.

$B_{12}H_{12}^{2-}$ and Me_2S_2 yield $B_{12}H_{11}SMe^{2-}$, $B_{12}H_{10}(SMe)_2^{2-}$ or $B_{12}H_9(SMe)_3^{2-}$, depending on reaction conditions, and $B_{12}H_{11}\,SH^{2-}$ can be obtained from $B_{12}H_{12}^{2-}$ and hydrogen sulphide. Sulphur dioxide reacts with $(H_3O)_2B_{12}H_{12}$ to produce $B_{12}H_{11}OH^{2-}$.

The reactions between $(H_3O)_2B_{10}H_{10}$ or $(H_3O)_2B_{12}H_{12}$ and olefins proceed readily to yield alkylated products of varying degrees of substitution, although in a few instances discrete compounds have been isolated.[977]

Reaction of tropenium bromide with $B_{10}H_{10}^{2-}$ leads to equatorially substituted $C_7H_6B_{10}H_9^-$ and a maroon product thought to be bis-equatorially substituted $(C_7H_6)_2B_{10}H_8$.[991–2] $B_{12}H_{12}^{2-}$ similarly yields $C_7H_6B_{12}H_{11}^-$. The anions show charge transfer absorptions at 439 nm ($C_7H_6B_{10}H_9^-$) and 349 nm ($C_7H_6B_{12}H_{11}^-$) in water and these are sensitive to solvent polarity.

The thermodynamics of proton dissociation in dilute aqueous solution of $[1,12\text{-}B_{12}H_{10}(COOH)_2]^{2-}$ have been studied and led to values of pK, ΔH° and ΔS° for the compound.[993]

Direct substitution of $B_{10}H_{10}^{2-}$ has also been achieved with aryldiazonium salts to give apically substituted $Ar{—}N{=}N{—}B_{10}H_9^{2-}$ derivatives. These species exhibit a charge-transfer band in the u.v. and visible spectrum which is affected by aryl substituent and solvent. The aryldiazonium derivatives can also be protonated at nitrogen and the pK_a values associated with the acid-base equilibrium are a linear function of Hammett's σ-values with a ρ-value of 1·7.[988]

A number of substituted $B_{10}H_{10}^{2-}$ ions have been prepared by indirect methods. $B_{10}H_8(N_2)_2$ treated with ammonia gave $B_{10}H_8(NH_3)_2$ which could be deprotonated by base to yield $B_{10}H_8(NH_2)_2^{2-}$.[978] $B_{10}H_8(CO)_2$ reacts with a variety of reagents to give substituted anions and analogous reactions are reported for $B_{12}H_{10}(CO)_2$. Thus reaction with MeOH yielded $B_{10}H_8(COOMe)_2^{2-}$, and with ammonia gave $B_{10}H_8(CONH_2)_2^{2-}$. Reduction with $LiAlH_4$ led to $B_{10}H_8Me_2^{2-}$[915] although $NaBH_4$ and $B_{10}Cl_8(CO)_2$ gave $B_{10}Cl_8(CH_2OH)_2^{2-}$.[984] Sodium azide reacted to form $B_{10}H_8(NCO)_2^{2-}$. Dehydration of $B_{10}H_8(CONH_2)_2^{2-}$ at 300° led to $B_{10}H_8(CN)_2^{2-}$.[915] $Me_2SB_{10}H_8SMe^-$ has been prepared by demethylation of $B_{10}H_8(SMe_2)_2$ with tributyl-phosphine.[914] Further substituted derivatives of the type $B_{10}Cl_8(CH_2X)_2^{2-}$ have been prepared from $B_{10}Cl_8(CH_2OH)_2^{2-}$ by treating it with a variety of reagents. Thus, the hydroxy-groups are acylated by acetic anhydride, or replaced by bromine and iodine on treatment with the corresponding halogen acid. The bromine atoms in $B_{10}Cl_8(CH_2Br)_2^{2-}$ are then readily replaced by a variety of nucleophiles e.g. CN^-, CH_2SOMe^-, OH^-, and the compound can be reduced to the dicarboxylic acid $B_{10}Cl_8(CH_2COOH)_2^{2-}$.[984] Other reactions of $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$ and their halogenated derivatives include preparations of acyl derivatives, e.g. $B_{10}H_8(COEt)_2^{2-}$ from organomercurial derivatives, reaction with NN-dimethylaniline to form $1,10\text{-}B_{10}Cl_8[COC_6H_4NMe_2]_2^{2-}$ and $B_{12}H_{10}[COC_6H_4NMe_2]_2^{2-}$, and even direct reaction between $B_{10}H_8(CO)_2$ and $B_{10}H_{10}^{2-}$ to form $B_{10}H_9COB_{10}H_8COOH^{4-}$ after working up in aqueous media.[985] The ketonic CO in the last species is extremely basic, so that invariably the protonated form $B_{10}H_9COHB_{10}H_8COOH^{3-}$ is isolated as salts. A number of analogous compounds have been isolated from similar reactions between substituted species, e.g.

$Me_2SB_{10}H_8COHB_{10}H_8COOH^{2-}$, $(Me_2S)_2B_{10}H_7COHB_{10}Cl_8COOH^-$,
$Me_2SB_{10}H_8COHB_{10}H_9^{2-}$ and $Me_3NB_{10}H_8COHB_{10}H_9^{2-}$.[985]

The indirect methods of substituting pseudohalides, which involve carbonyl derivatives of the polyhedral boranes, led to a maximum of two pseudohalogen substituents per boron polyhedron. Further substitution has been achieved by photoinduced nucleophilic substitution in halogenated polyhedral borane anions.[994–5] Thus, prolonged irradiation of $B_{12}Br_{12}^{2-}$ in the presence of CN^- gave $B_{12}Br_3(CN)_9^{2-}$, or with further extended irradiation, $B_{12}Br_2(CN)_9H^{2-}$ and $B_{12}Br(CN)_9H_2^{2-}$. The last species was also obtained from prolonged irradiation of $B_{12}Br_{10}H_2^{2-}$ in the presence of cyanide ion. Exhaustive irradiation of $B_{12}Cl_{12}^{2-}$ led only to $B_{12}Cl_5(CN)_7^{2-}$, whereas $B_{10}Cl_{10}^{2-}$ yielded mixtures of $B_{10}Cl_9CN^{2-}$, $B_{10}Cl_8(CN)_2^{2-}$, $B_{10}Cl_7(CN)_3^{2-}$ and other products.[995] Short irradiation of $B_{12}Br_{12}^{2-}$ in the presence of azide ion led to $B_{12}Br_{11}N_3^{2-}$ and $B_{12}Br_{10}(N_3)_2^{2-}$, although no product was isolated from prolonged irradiation, and similar results were noted for the cyanate ion.[995] Other substitutions have been patented.[996]

The generation of hydrogen by hydrolysis of a Pt–$B_{12}H_{12}^{2-}$ reaction has been patented.[997]

The photolysis of a solution of the cæsium salt of 1-iodobenzenenonahydrodecaborate(1−), $B_{10}H_9IC_6H_5^-$, has yielded $B_{10}H_9I^{2-}$, benzene, and other products.[997a]

In the mass spectrum of $B_{10}H_8(N_2)_2$ there is less boron fragmentation than from $B_{10}H_{14}$. Prominent ions were $B_{10}H_8N_4^+$ and $B_{10}H_8N_2^+$ with no evidence of similar ions with fewer than eight hydrogen atoms.[998]

(ii) OXIDATIONS OF POLYHEDRAL IONS AND THEIR DERIVATIVES

The polarographic oxidation of $B_6H_6^{2-}$, $B_8H_8^{2-}$ and $B_9H_9^{2-}$ ions has been studied.[42] The anions are quite comparable in oxidative stability with half-wave potentials of $-0{\cdot}33$, $-0{\cdot}15$ and $-0{\cdot}04$ V respectively for the ions $B_6H_6^{2-}$, $B_9H_9^{2-}$ and $B_8H_8^{2-}$. A value of $+0{\cdot}2$ V for the half-wave potential in the oxidation of $B_{11}H_{11}^{2-}$ was reported under slightly different conditions from those of the smaller ions.[53] $B_{10}H_{10}^{2-}$ has a half-wave potential for oxidation of $+0{\cdot}85$ V. $B_{12}H_{12}^{2-}$ is not oxidized at $+1{\cdot}4$ V versus a standard calomel electrode but shows an anodic oxidation wave at $+1{\cdot}50$ V in acetonitrile.[199, 999]

Aerial oxidation of $B_9H_9^{2-}$ has been used to generate $B_6H_6^{2-}$, $B_7H_7^{2-}$, $B_8H_8^{2-}$ and the intermediate $\cdot B_8H_8^-$.[42] Oxidation of $B_{10}H_{10}^{2-}$ with species such as Fe^{3+} or Ce^{4+} has been shown to lead to coupling of the polyhedral species, forming $B_{20}H_{18}^{2-}$ or $B_{20}H_{19}^{3-}$; these have been discussed[186, 187, 892–6] in Part 7. Oxidation of $B_{10}H_{10}^{2-}$ with anhydrous cupric chloride has been reported to produce free radicals, and the possible gross reaction sequence is[1000]:

$$2CuCl_2(s) + K_2B_{10}H_{10}(s) \xrightarrow{\text{ether}} 2KCl(s) + CuCl(s) + HCl + CuB_{10}H_9$$
$$CuCl_2(s) + CuB_{10}H_9 \longrightarrow 2CuCl(s) + (B_{10}H_9)$$

An early report of the reaction of $B_{10}H_{10}^{2-}$ with nitrogen dioxide, NO_2, indicated that nitroso-derivatives could be prepared[1001], but *X*-ray examination of the product showed it to be $B_{20}H_{18}NO(NHEt_3)_3$.[1002] Subsequent work showed that oxidation of $B_{10}H_{10}^{2-}$ by nitrogen dioxide proceeded through a red intermediate to the blue $B_{20}H_{18}NO^{3-}$ and that, unless conditions were carefully chosen, higher nitrosated ions would be obtained.[1003] The $B_{20}H_{18}NO^{3-}$ ion was further shown to be stable towards oxidants and bases; the NO group could be reduced to NH_2 by hydrogen and Raney nickel. The $B_{20}H_{18}NO^{3-}$ ion was halogenated by all the halogens, and species isolated included $B_{20}H_2Cl_{16}NO^{3-}$, $B_{20}H_{14}Br_4NO^{3-}$, $B_{20}H_{11}I_7NO^{3-}$ and $B_{20}H_{10}F_8NO^{3-}$.[1003]

$B_{10}H_{10}^{2-}$ is completely oxidized to boric acid at room temperature by potassium permanganate at pH 7. It is suggested that the reaction proceeds by the replacement of cage hydrogens by hydroxyls followed by extensive decomposition.[908, 1004]

Electrochemical oxidation of $B_{12}H_{12}^{2-}$ in MeCN yields $B_{24}H_{23}^{3-}$ which consists of two $B_{12}H_{12}^{2-}$ units with one bridging proton in common. The $B_{24}H_{23}^{3-}$ ion reacted with iodine at room temperature to yield 1,1′-μ-hydro-bis(7-iododecahydro-*closo*-dodecaborate)(3−), $B_{24}H_{21}I_2^{3-}$. Bromination under a variety of conditions gave

$B_{24}H_{23-n}Br_n^{3-}$ ($n=7$, 10, 11) and $B_{24}H_{22-n}Br_n^{4-}$ ($n=11$, 14, 18). Exhaustive chlorination in water gave $B_{24}H_4Cl_{18}^{4-}$ with no evidence of decomposition.[199, 894, 999]

B. Further Chemistry of Linked *closo*-Polyhedral Ions

$B_{20}H_{18}^{2-}$ and its photo-isomer are reduced by active metals such as sodium or magnesium to $B_{20}H_{18}^{4-}$. The reaction of $B_{20}H_{18}^{2-}$ with hydroxide was originally thought to produce $B_{10}H_9OH^-$ [1005] but later work showed that the species produced was, in fact, $B_{20}H_{17}OH^{4-}$, which may be considered as a substituted derivative of the $B_{20}H_{18}^{4-}$ ion.[186, 1006–7] Similarly, reaction of $B_{20}H_{18}^{2-}$ with methoxide leads to $B_{20}H_{17}OMe^{4-}$.[186] The product of the reaction of aqueous hydroxide ion with $B_{20}H_{18}^{2-}$ is an isomer of $B_{20}H_{17}OH^{4-}$ whose 64 MHz ^{11}B n.m.r. spectrum shows similarity to the ae isomer of $B_{20}H_{18}^{4-}$, and is compatible only with a structure which has an equatorial hydroxyl substituent. Of the possible isomers, the structure preferred is shown in Fig. 9.1.[1007]

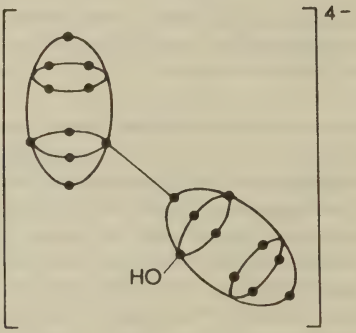


Fig. 9.1

This isomer is thermodynamically less stable than the product to which it is converted under equilibrium conditions, and this second isomer is thought to have the structure shown in Fig. 9.2.

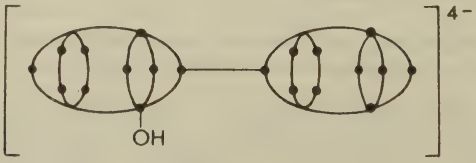


Fig. 9.2

Potentiometric titration of either isomer results in the formation of $B_{20}H_{18}OH^{3-}$, and spectroscopic evidence suggests that this comprises two B_{10} polyhedra joined by an apical-equatorial B–H–B bridge with the hydroxyl group at an equatorial position.[1007] The kinetics of the reaction of hydroxide are represented by:

$$\text{Rate} = k_1[B_{20}H_{18}^{2-}] + k_2[OH^-][B_{20}H_{18}^{2-}]$$

and a mechanism for the reaction was proposed.

Hydroxyl ion also reacts with $B_{20}H_{16}L_2$ compounds to form $B_{20}H_{16}L_2(OH)^-$ and $B_{20}H_{15}L_2(OH)^{2-}$, and an acid–base equilibrium exists between the two substituted anions. N-chloro- and N-bromo-succinimide react with $B_{20}H_{18}^{2-}$ to yield partially substituted derivatives, e.g. $B_{20}H_{12}Cl_6^{2-}$ and $B_{20}H_{13}Br_5^{2-}$; similar reactions with $B_{20}H_{17}OH^{4-}$ yield $B_{20}H_4Br_{13}OH^{4-}$.[186]

C. Further Properties of the *nido*-Anions

In contrast with *closo*-polyhedral anions, the substitution of the *nido*-anions has rarely been reported. The only examples in the literature are the postulated species $Me_3NH^+B_5H_7Et^-$, which was isolated from the reaction of 1-ethylpentaborane(9) with NMe_3[589], and possible reaction products of alkylated pentaboranes with sodium hydride.[591]

The bulk of the chemistry of the *nido*-anions has concerned reactions of the alkali-metal salts of the hydroborate anions with element–halogen systems or diborane. Thus, alkali-metal salts of $B_5H_8^-$ react with DCl to give bridge-deuterated B_5H_9[472], or with Me_3SiCl to yield bridge-substituted μ-$Me_3SiB_5H_8$[646], which slowly isomerizes at room temperature to 2-$Me_3SiB_5H_8$. The μ-$Me_3SiB_5H_8$ may be brominated to give 1-Br-μ-$Me_3SiB_5H_7$. Similarly, LiB_5H_8 reacts with derivatives of the type R_2PCl to yield substituted pentaboranes.[647–8] Bridge substitution occurs with Me_2PCl to yield μ-$Me_2PB_5H_8$ or $Me(CF_3)PCl$ to give two isomers of μ-$Me(CF_3)PB_5H_8$, although curiously $(CF_3)_2PCl$ leads to 1-$(CF_3)_2PB_5H_8$.[647] $B_5H_8^-$ reacts with B_2H_6 to yield an isomer of B_6H_{10} which converts to normal B_6H_{10} on standing at room temperature. More vigorous conditions lead to $B_{10}H_{14}$.[106] Bridge-substituted pentaboranes are also formed from R_3GeX, R_3SnX[646, 649, 650], and R_2BX species.[651]

No reactions of the $B_6H_9^-$ ion have been reported.

The tetramethylammonium derivative of the ion of empirical formula $B_8H_{12}^-$ yields B_8H_{14} on treatment with HCl at −78°.[132]

The $B_9H_{14}^-$ ion reacts with hydrogen chloride at −80° to form *i*-B_9H_{15}[143], although a similar reaction with polyphosphoric acid at room temperature yields B_6H_{10} and B_8H_{12}, presumably as a result of decomposition of first-formed *i*-B_9H_{15}.[473] Aqueous ethanolic solutions of CsB_9H_{14} react with simple salts of Cu^{II}, Ag^{I} and Au^{III} in presence of excess of triphenylphosphine to form complexes of general stoichiometry $(Ph_3P)_3MB_9H_{14}$, and similar complexes $(Ph_3P)_3MB_9H_{12}S$ are formed with the $B_9SH_{12}^-$ species.[168] These compounds appear to be ionic, and attempts to prepare covalent derivatives of the type $(Ph_3P)_2MB_9H_{14}$ were not wholly successful. The $B_9H_{12}S^-$ ion reacts with Ph_2PCl to form $Ph_2PH,B_9H_{11}S$.[82]

The $B_{10}H_{12}^{2-}$ ion has been shown to act as an effective chelating ligand in a number of products of reactions of zinc, cadmium and mercury alkyls and halides with decaborane(14).[65, 696, 1008–9] Thus diethylcadmium reacts with decaborane(14) to form $CdB_{10}H_{12},2L$ ($L = Et_2O$, THF) which reacts with ethereal hydrogen chloride to regenerate $B_{10}H_{14}$, and ionize in aqueous solution to give $[(B_{10}H_{12})_2Cd]^{2-}$.[65]

$$R_2Cd + B_{10}H_{14} \xrightarrow[\text{solvent L}]{\text{ethereal}} CdB_{10}H_{12},2L + 2RH$$

$$CdB_{10}H_{12},2L + 2HCl \xrightarrow{\text{ether}} B_{10}H_{14} + CdCl_2 + 2L$$

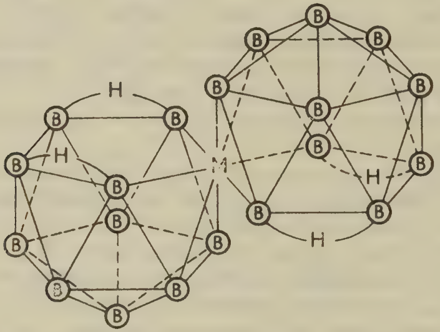
$$2CdB_{10}H_{12},2L \xrightarrow[\text{solvent}]{\text{hydroxylic}} Cd^{2+}[Cd(B_{10}H_{12})_2] + 2L$$

Similar reactions occur with diorganozinc derivatives to yield $[(B_{10}H_{12})_2Zn]^{2-}$.[1009]

The most extensively investigated ion is undoubtedly $B_{10}H_{13}^-$. Much work has been carried out on $NaB_{10}H_{13}$, but decaboranylmagnesium iodide has also been used. Sodium tridecahydrodecaborate(1−) reacts with a variety of element–halogen derivatives to give substituted decaborane(14) derivatives. Thus reaction with alkyl halides yielded decaborane(14) derivatives alkylated at the 6-position.[725, 906] Reaction with olefins gave alkyldecaboranes[1010], and reaction with diphenylchlorophosphine gave $Ph_2PB_{10}H_{13}$, which was degraded by alcohols to $B_9H_{13}PH(Ph)_2$.[1011–12] Reactions of decaboranyl-magnesium iodide were slightly different in that alkylated products were observed only with alkyl fluorides, alkyloxonium fluoroborates, or dialkylsulphates.[638–40] However, reaction of $B_{10}H_{13}MgI$ with Ph_2PCl gave $Ph_2PB_{10}H_{13}$, which readily functioned as a strong monoprotic acid to give the hydrolytically stable ion $Ph_2PB_{10}H_{12}^-$, although titration with base in aqueous methanol gave $B_9H_{13}PH(Ph)_2$.[909] Similar reactions of $B_{10}H_{13}MgI$ with a variety of nitrogen, phosphorus, arsenic and antimony halide derivatives have been patented.[1013]

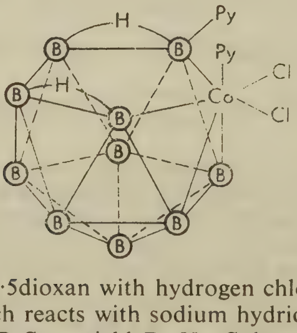
The $B_{10}H_{13}^-$ ion has been shown to react with a variety of transition metal–halide derivatives. Reactions with excess of Ph_3P and CuCl, AgCl or AuCl have given species $(Ph_3P)_3MB_{10}H_{13}$ which are essentially ionic in nature.[168] However reaction of excess of $B_{10}H_{13}^-$ with $(Ph_3P)_2NiCl_2$, $(Et_3P)_2PtCl_2$, $(R_3P)_2PdCl_2$ and $(Ph_3P)_2IrCoCl$ have given essentially covalently bonded chelates, e.g. $[M(B_{10}H_{12})_2]^{2-}$, $M(B_{10}H_{12})L_2$ and $M(B_{10}H_{12})L_3^-$.[1014–15]

There has been some discussion regarding the structure of $B_{10}H_{12}^{2-}$ derivatives of the type $M(B_{10}H_{12})_2^{2-}$. The structures originally postulated for the zinc, cadmium and mercury derivatives were based on a 6,9-metal bridged decaborane skeleton[65, 696, 1008–9] but recent *X*-ray crystallographic studies[189a] have shown that the metal atoms are shifted off the C_2 axis, as shown on p. 258. The neutral cadmium complex is dimeric, as shown on p. 299.[65a] The transition-metal derivatives are also derived from fused eleven-particle icosahedral fragments[189b, 1015]:

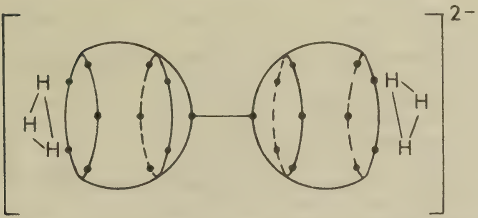


Sodium tridecahydrodecaborate(1 –) also reacts with iodine in dialkylethers to yield alkoxydecaborane derivatives.[839] $B_{10}H_{13}^-$ also undergoes an unusual boron exchange reaction with diborane(6), which appears to involve an intermediate $B_{11}H_{16}^-$ species.[1016]

The reactions of $Me_4NB_{10}H_{13}$ and $Et_3NHB_{10}H_{13}$ are somewhat different from those of $NaB_{10}H_{13}$. Mercury(II) chloride reacted directly to produce $(Me_4N)_2[Hg(B_{10}H_{12})_2]$, and bispyridinecobalt(II) halides gave the compound $(Me_4N)[pyCoCl_2B_{10}H_{11}py]$ whose structure was thought to be as shown[903]:



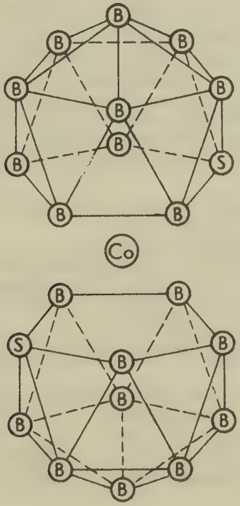
Treatment of $NaB_{11}H_{14}$,2·5dioxan with hydrogen chloride has been reported to yield $B_{11}H_{15}$,2·0dioxan which reacts with sodium hydride to regenerate $NaB_{11}H_{14}$, and with water, ROH, or R_2S to yield $B_{11}H_{13}$,Solvate.[1017] Recent workers have found that protonolysis of $B_{11}H_{14}^-$ in dioxan leads to *n*-$B_{18}H_{22}$.[1018] The reaction between $NaB_{11}H_{14}$,2·5dioxan and mercury(II) bromide in tetrahydrofuran solution leads to the novel linked dianion $B_{22}H_{26}^{2-}$ which, on the basis of its i.r. and n.m.r. spectra, is thought to have the structure of two B_{11} units linked by a direct B–B bond at the apex position[1019]:



When the oxidation is carried out in aqueous solution the product is the $B_{11}H_{13}OH^-$ ion. Both anions were isolated as tetramethylammonium salts and it was shown that $(Me_4N)_2B_{22}H_{26}$ is a 2:1 electrolyte and $Me_4NB_{11}H_{13}OH$ is a 1:1 electrolyte in acetonitrile.

The $B_{11}H_{13}^{2-}$ ion reacts with $PhPCl_2$ to complete the icosahedron and form $B_{11}H_{11}PPh$.[83] Similarly, $Na_3B_{10}H_{10}CH,2THF$ reacts with phosphorus trichloride to form initially the 1,2-isomer of $B_{10}H_{10}CHP$, which rearranges on heating to the 1,7-isomer.[83] $B_{11}H_{14}^-$ also reacts with a number of species of the type $(R_3P)_3MCl$ where M = Cu, Ag, Au to give essentially ionic derivatives.[168]

Freshly prepared $B_{10}H_{10}S^{2-}$ reacts readily with $PhBCl_2$ to give the icosahedral $PhB_{11}H_{10}S$, which is converted by strong base to $PhB_{10}H_{10}S^-$. Reaction of the latter with BuLi followed by further $PhBCl_2$ leads to $Ph_2B_{11}H_9S$.[82] Reaction of $B_{10}H_{10}S^{2-}$ with a range of transition metal halides gives a series of sandwich compounds. Thus reactions of $B_{10}H_{10}S^{2-}$ with $FeCl_2$ or $CoCl_2$ yields $[(B_{10}H_{10}S)_2Fe^{II}]^{2-}$, or $[(B_{10}H_{10}S)_2Co^{III}]^-$. Other compounds which have been obtained are: $(B_{10}H_{10}S)CoC_5H_5$, $(B_{10}H_{10}S)Pt(Ph_3)_2$, $(B_{10}H_{10}S)Co(PEt_3)_2$, $(B_{10}H_{10}S)Re(CO)_3^-$ and $[(B_{10}H_{10}S)_2Fe^{III}]^-$.[82] The proposed structures involve sandwich structures of the type found in a number of carborane anion–metal complexes. (For a review, see M. F. Hawthorne, *Accounts of Chem. Res.*, 1968, **1**, 281.) Thus, the proposed structure of $[(B_{10}H_{10}S)_2Co]^-$ is:



It can be seen that an extensive coordination complex chemistry of polyhedral boranes is beginning to develop, and that the general area of metalloborane compounds promises to become as structurally diverse and mechanistically intriguing as its counterpart in organometallic chemistry. If this promise is fulfilled, the chemistry of the boron hydrides will develop even more dramatically during the next two decades than it has done during the past twenty years. The associated problems of describing the bonding in these novel cluster compounds will, no doubt, be formidable, but the possibility for devising catalytically controlled conversions to compounds with desirable properties is immense.

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NOTE ADDED IN PROOF (6th MAY 1980)

Since this Section was completed in 1970 there have been many major advances in the chemistry of the higher boranes and their derivatives. Several new boranes have been synthesized and characterized, *arachno-* and *hypho*-boranes have been recognized, the field of metalloboranes has burgeoned, and the general principles known as Wade's Rules have provided valuable guidelines for systematizing of the whole field. Various aspects of these new results have been summarized in the following books and reviews.

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SECTION B6

ALKALI-METAL HYDROBORATES

BY D. E. BUCK

INTRODUCTION

This review of the chemistry of the alkali-metal hydroborates is limited arbitrarily to their inorganic aspects. Their use in organic chemistry, primarily as reducing agents, is reviewed in Refs. 50, 51, 196, 342, 353, 468, 495 and 537. Various other topics are reviewed in Refs. 276, 368c, 445, 512, 584 and 590. The reactions of alkali-metal hydroborates are dealt with by Ref. 423, and the physical and chemical aspects of metal hydroborates by Refs. 5, 268 and 492. Reference 268 is the most recent and complete, particularly in the description of chemical reactions of hydroborates with other inorganic compounds; Ref. 5 is an updated and more complete version of Ref. 492.

The nomenclature used here generally conforms to the recommendations of the Advisory Sub-Committee on the Nomenclature of Boron Compounds, published in 1968 and described in Ref. 426. The term 'tetrahydroborate' (shortened, when clarity is not sacrificed, to 'hydroborate') designates a compound containing the BH_4^- species. The terms 'borohydride' and 'boronat' have been previously used in the English and German languages, respectively.

PROPERTIES OF ALKALI-METAL TETRAHYDROBORATES

General Properties

In this section we deal with those properties, particularly thermodynamic and electrochemical, which pertain generally to the BH_4^- species: specific properties, including thermodynamic properties, of the various alkali-metal tetrahydroborates will be discussed below under headings referring to the individual compounds.

Values of the polarization of the tetrahydroborate ion in the various alkali-metal salts (in Å^3) calculated from the refractive index are as follows:

$NaBH_4$	4·02 (λ = Na_D)[17]	4·06 (white light)[552]
KBH_4	3·92 (λ = Na_D)[17]	3·96 (white light)[552]
$RbBH_4$	3·98 (λ = Na_D)[17]	3·94 (white light)[552]
$CsBH_4$	3·81 (λ = Na_D)[17]	3·78 (white light)[552]
Average	3·9±0·1	3·94±0·07

The relative constancy of this value is expected for essentially ionic crystals. For the aqueous ion, the standard free energy of formation ΔG°_f at 298 K is 28·6 kcal mol^{-1},[552] the standard entropy S° is 25·5,[19, 552] 26·3[221] cal deg^{-1} mol^{-1} and the standard heat of formation ΔH°_f is 12·4,[552] 10·4[221] kcal mol^{-1}. The heat and entropy of hydration of the ion at 298 K are 72±5 kcal mol^{-1} and -13 cal deg^{-1} mol^{-1}, respectively.[17, 19] At 240 K in liquid ammonia, the heat of formation ΔH°_f is $-17{\cdot}2$ kcal mol^{-1}, the partial molal entropy is $-18{\cdot}4$ cal deg^{-1} mol^{-1} and the free energy of formation ΔG°_f is 6·2 kcal mol^{-1}.[92] From the additivity of heat capacity, the standard heat capacity in a crystal is calculated for BH_4^-.[321] The BH_4^- species has been observed in a mass spectrometer.[254] The entropy of vaporization of the ion from salts of the monovalent cations was calculated to be 29·5 cal deg^{-1} mol^{-1},[18] and a calculation by statistical mechanics has been made of the gaseous entropy.[619] The heat of formation ΔH°_f at 298 K of the gaseous ion is -23 ± 5 kcal mol^{-1}.[17] The usual thermodynamic functions are tabulated for the region 200–2000 K.[17] At 25°C the equivalent conductance of BH_4^- in water is $\lambda BH_4^- = 80 \pm 3$ ohm^{-1} cm^2 equiv^{-1}; this value was derived from the conductance of the potassium salt (Λ_0 (KBH_4) $= 153 \pm 3$ ohm^{-1} cm^2 equiv^{-1}) in 0·1M potassium hydroxide solution. The hydroborate ion has a conductance very close to that of Br^- and I^- ions (78·2 and 76·9).[551] The anodic behaviour was examined with platinum electrodes and gave a potential, −0·87 V, arising from a two-electron partial ionization of the BH_4^- ion. Following space-charge polarization of the anode, further hydrogen ionization is accompanied by hydrolysis and hydrogen evolution.[136] Other electrodes failed to give a stable potential.[135–6] The oxidation-reduction potential of $NaBH_4$ is −1·23 V in both acid and alkaline media.[408]

The polarographic behaviour of the BH_4^- ion is confined to a single wave at −0·65 V (against a normal calomel electrode). The half-wave potential is not a function of the cation (Li^+, Na^+, K^+ or Cs^+)[396–8], pH, temperature (15–35°C)[398] or concentration of the supporting electrolyte (lithium, sodium or potassium hydroxide) or the BH_4^- ions.[396] The magnitude of the wave is, however, linearly proportional to the BH_4^- concentration in the region 10^{-1}–10^{-3} molar.[396] At pH 12·5, the ion is stable to hydrolysis[200] and the wave disappears. The reaction is then due not to the ion itself but to a hydrolysis product, postulated as $BH(OH)_3^-$ [396–8] or BH_3OH^-.[195]

$$BH(OH)_3^- + OH^- \rightarrow BO_2^- + 2H_2O + H + e$$
$$BH_3OH^- + 3OH^- \rightarrow BO_2^- + \tfrac{3}{2}H_2 + 2H_2O + 3e$$

Vibrational Spectra

The infra-red spectrum of the BH_4^- ion in the solid state is reported in references 43, 296, 455–6, 519–20, 617 and 49. Lithium hydroborate has bands at 2,320 and 1,096 cm^{-1}, resulting from B—H stretching and in-plane H—B—H bending, respectively. Sodium hydroborate has similar bands at 2,270 and 1,080 cm^{-1}. Both crystals have combination bands in the region 3,250–3,400 cm^{-1}.[455–6] An 'anomalous' band, appearing at 1,290 cm^{-1} in the lithium hydroborate spectrum, is explained as a band normally inactive in the infra-red whose degeneracy has been removed by the symmetry (C_s) of the crystalline field at the BH_4^- site.[49, 519] The spectra are those of the tetrahedral BH_4^- ion, and the slightly higher B—H stretching frequency of the lithium salt indicates an ionic bonding less complete than that of the sodium salt.[455] At liquid-nitrogen temperatures, the bands of sodium hydroborate are shifted to 2,298 and 1,121 cm^{-1}.[253] At −182°C the spectrum of a thin film of sodium hydroborate shows shifts from thermal contraction of the lattice, and the band derived from the bending mode is split into three bands.[520] The order–disorder transition of sodium hydroborate at −83°C is correlated with the infra-red spectrum, and a change in lattice type is noticed.[296] The tetrahydroborate ion substituted in alkali-halide lattices has been studied[295, 297, 457–8, 526] and the variations arising from the lattice parameters of the solvent halides have been discussed.[295] Because the frequency shifts cannot be explained by long-range forces, short-range forces must be the determining factor.[526]

Assignments of the frequencies of fundamental vibration modes have been made on the basis of Raman spectra in liquid ammonia at −50°C; a tetrahedral configuration belonging to the T_d point group is assumed.[48, 80, 142, 563, 617] Table I gives the assignments for the species measured. Although there are small shifts in the bands of the different salts, possibly related to the polarizing ability of the cation, there are no spectral features to suggest a solvent–solute interaction.[142] Vibrational frequencies and assignments have been made for $Li^{11}BH_4$, $Na^{11}BH_4$, $K^{11}BH_4$, $Li^{10}BH_4$ and $Na^{10}BH_4$ (and corresponding deutero-compounds) in liquid ammonia and deuterated ammonia.[142]

Assignments for tetrahedral configuration for an ion belonging to the T_d point group:

ν_1	(Raman)	Totally symmetric stretching mode
ν_2	(Raman)	Doubly degenerate bending mode
ν_3	(IR)	Triply degenerate stretch mode
ν_4	(IR)	Triply degenerate bonding mode

are given in Table I.

Table I.—Vibrational Frequency Assignments, BH_4^- in Liquid NH_3 (cm^{-1})[142]

$Li^{11}BH_4$	$Na^{11}BH_4$	$K^{11}BH_4$	$Li^{10}BH_4$	$Na^{10}BH_4$	Assignments
1,082	1,080	1,084	1,085	1,093	ν_4
1,202	1,210	1,213	1,206	1,208	ν_2
2,146	2,146	2,154	2,150	2,161	$2\nu_4$
	2,242			2,250	ν_3
2,265	2,264	2,266	2,268	2,270	ν_1
2,402	2,398	2,404	2,409	2,405	$2\nu_2$

Force constants have been calculated[43, 80, 100, 439, 616–17] and show a monotonic increase for the isoelectronic series BH_4^-, CH_4, NH_4^+,[616–17] and a calculated B—H distance of 1·175 Å.[80] A normal coordinate analysis has been used to calculate the potential constants and anharmonicity factors for BH_4^-, BD_4^-, $^{10}BH_4^-$, $^{10}BD_4^-$ [572] and potential constants have been evaluated by means of a group-theoretical treatment of infra-red and Raman date.[462, 573]

N. M. R. Spectra

The proton magnetic resonance of sodium tetrahydroborate, resolved at 40 MHz, shows a superimposed intense quadruplet and a weaker septet. The former set, with its components of equal intensities, arises from coupling with ^{11}B, $J = \frac{3}{2}$ and abundance of 80%, and the latter from coupling with ^{10}B, $J = 3$ and abundance of 20%.[429] The ^{11}B resonance at 6 MHz is split, through spin–spin coupling with four tetrahedrally situated protons, into five groups of lines of relative intensity 1, 4, 6, 4, 1.[429] The B—H spin–spin coupling constant is 82 Hz for $NaBH_4$ in water[429, 434] and 81 Hz in 0·1M aqueous sodium hydroxide[451], while for $LiBH_4$ in diethyl ether a value of 75 Hz is found.[434] The chemical shift of aqueous $NaBH_4$ is 38·7 p.p.m., while $LiBH_4$ in ether records 38·2 p.p.m., both relative to boron trifluoride etherate.[434]

Resonances of ^{11}B and ^{23}Na in solid $NaBH_4$ at 23°C are both sharp with no satellites, indicating a symmetric BH_4 tetrahedron with no Na—B coupling.[527] The ^7Li resonance in solid $LiBH_4$ shows no structure from $+68$ to -76°C, a result of an essentially zero field gradient at the lithium site.[252, 435] Proton resonance in solid Na, K and Rb tetrahydroborates allows calculation of a B—H bond distance of $1{\cdot}255 \pm 0{\cdot}02$ Å[179], in good agreement with the neutron diffraction value of 1·260.[448] The X—H coupling constant shows a linear relationship with atomic number in the isoelectronic series BH_4^-, CH_4, NH_4^+.[464] The potential barrier to BH_4^- rotation in the crystal, as calculated from the temperature variation of the second moment, is 2·4, 3·8 and 3·9 kcal mol^{-1} for the Na, K and Rb salts, respectively.[179]

Theoretical Aspects

The tetrahedral configuration of the hydroborate ion, approximating spherical symmetry, establishes it as a member of a class of molecules and ions which have been the subject of much theoretical treatment. One-centre wave-functions have been calculated[9, 10, 34, 218] and used to derive, among other parameters, diamagnetic susceptibility, electric polarizability[9, 218], molecular energy, bond length, and force constant for the symmetric stretching modes.[9] Approximate Hartree-Fock calculations have led to values of interatomic distances and energy of the BH_4^- ion.[320] The atomic valence state and interatomic resonance energies have been calculated for B^-, in BH_4^-.[140] LCAO–MO resonance studies of BH_4^- give energies of filled orbitals[246]; an optimization of an LCAO–SCF wave-function gives an electron-density map and a derived Mulliken charge of $+0{\cdot}044$ for the boron and $-0{\cdot}261$ for the H atom.[238] That the net negative charge resides on the proton is also shown by a modified Hückel calculation of electronic structure.[292] An LCAO–MO approximation has been used to predict, in good agreement with measured values, the nuclear-spin coupling constants between the atoms.[453] Calculations have been made for the degree of orbital hybridization and bond polarization[557], force constants[100, 565], and Coriolis coupling in rotation-vibration of symmetric tetrahedral molecules including BH_4^-.[100]

LITHIUM TETRAHYDROBORATE ($LiBH_4$)

Structure

X-Ray diffraction measurements have shown that lithium hydroborate has an orthorhombic unit cell containing four molecules and having the dimensions $a = 6{\cdot}81$ Å, $b = 4{\cdot}43$ Å and $c = 7{\cdot}17$ Å.[228] A calculated density of 0·66 g cm^{-3} agrees with the measured value of 0·666 g cm^{-3}.[228] The arrangement of lithium and tetrahydroborate ions satisfies the space group *Pcmn*. The protons are tetrahedrally disposed about the B atom and each lithium is surrounded by four hydroborate ions; two Li—B distances are 2·56 Å and two are 2·47 Å. The spatial distribution of nearest-neighbour protons about the Li atom is roughly tetrahedral, where each proton belongs to a different hydroborate ion. The angles between the Li and B atoms vary from 97° to 116°.[228] The symmetry of the perturbing crystalline field removes the degeneracy of the hydroborate vibrational levels, which become infra-red active; this explains an 'anomalous' infra-red band at 1,250 cm^{-1}.[49, 519] The band associated with B—H valence vibration at about 2,300 cm^{-1} is at a slightly higher frequency than that of the sodium salt, a completely ionic species. A lesser degree of ionic bonding in lithium tetrahydroborate is postulated to account for the difference.[455] Calculation of the degree of ionic character of lithium hydroborate shows it to be about half that of caesium perchlorate.[510]

Studies of ^7Li by n.m.r. show no splitting and a zero field-gradient at the Li nucleus. Deuteron resonance of $NaBD_4$ showed no splitting to −160°C, and no structure was seen in the ^{11}B resonance. The BD_4^- ion is thought to be in rapid re-orientation at temperatures as low as −160°C.[435]

The overall structure may be thought of as strings of hydroborate tetrahedra stacked edge on edge along the *b* direction.[228] This structure is unique in the alkali-metal hydroborates, where the rule is a sodium chloride-type lattice at room temperature.[1]

Properties

Lithium hydroborate is a salt-like[496, 510], hygroscopic[504], crystalline material with a reported melting point of 275°C[496] or 278°C[613] and density 0·681 g cm^{-3} [108] or 0·66 g cm^{-3} [228] at 25°C. At 0°C, its vapour pressure is much less than 10^{-5} Torr, and the salt neither decomposes nor sublimes.[496] Thermal analysis (DTA) has shown four temperature regions in which the compound undergoes detectable change of state.[170] The first (108–112°C) is reversible and is thought to correspond with a polymorphic transformation. At the second (268–286°C), fusion occurs with a hydrogen loss of less than 2% by weight. Decomposition occurs at about 380°C with hydrogen evolution and little indication on the DTA trace. A fourth region (483–492°C) is unexplained. All the thermal effects, except the third, are endothermic. The heat of decomposition (to lithium hydride, boron and hydrogen) is calculated to be +24·70 kcal mol^{-1} [529] at 25°C. The lattice energy of the crystalline compound is estimated from heats of formation to be 186 kcal mol^{-1}.[17]

The heat of formation of the compound has been measured[108], and the heat capacity determined from 15 to 303 K.[225] The usual thermodynamic functions have been tabulated for 15 to 300 K[225] and 0 to 2000 K (for a hypothetical solid).[269] At 298·16 K, the values are as follows[144]:

$$\begin{aligned} \Delta H^\circ_f &= -46{\cdot}44 \text{ kcal mol}^{-1} \\ \Delta G^\circ_f &= -30{\cdot}80 \text{ kcal mol}^{-1} \\ S^\circ &= 18{\cdot}13 \text{ cal deg}^{-1}\text{ mol}^{-1} \\ C^\circ_p &= 19{\cdot}73 \text{ cal deg}^{-1}\text{ mol}^{-1} \end{aligned}$$

Solubilities and Solvates

Solubilities of lithium hydroborate in a number of solvents are shown in Table II. Solvent–solute complexes, described below, are formed with these solvents.

Table II.—Solubility of $LiBH_4$

Solvent	Temp. (°C)	Solubility (g per 100g solvent)	Reference
$(CH_3)_2O$	−45·2	1·6	482
$(C_2H_5)_2O$	25	4·28	317, 22
	−112	0·20	317
	−63	0·41	317
	−23	0·73	317
	0	1·28	317, 22
	15	2·32	317, 22
$(CH_2)_4O$	25	28	139
	25	22·2	318
	−22·9	15·5	318
	0	17·8	318
	35	24·3	318
$(—O—(CH_2)_2—)_2$		0·3	532

Pressure–composition isotherms from −78·6 to +20°C show the existence of three dimethyl etherates with molar hydroborate : ether ratios of 2 : 1, 1 : 1 and 1 : 2. The dissociation (to hydroborate and ether) pressures, heats, free energies and entropies of dissociation along with the heats, free energies and absolute entropies of the etherates have been determined for the region −63 to 57°C. The dimethyl etherates are stable only below room temperature: their respective vapour pressures are 12·8 Torr at 20°C, 33·2 Torr at 20°C and 601·9 Torr at 17·1°C.[482] Pressure–composition isotherms of the diethyl etherates from −63·5 to 25°C show a mono- and hemietherate which can be dissociated in vacuum at room temperatures.[281, 317, 504] The dissociation pressures as functions of temperature, along with a set of thermodynamic functions similar to those listed for the methyl etherate, have been determined.[317] The dissociation pressures are: monoetherate 60·6 Torr at 19·8°C; hemietherate 46·5 Torr at 25·3°C. The heats of solution of lithium tetrahydroborate and its diethyl etherates in diethyl ether have also been determined.[317] At 25°C in diethyl ether solution, deviations from Raoult's law indicate a state of hydroborate aggregation of 1·8 at a lithium hydroborate diethyletherate mole fraction of 0·014, and a solute aggregation of 3·3 at mole fraction 0·175.[317] A dimeric species $Li[Li(BH_4)_2]$ has been proposed.[317] In di-*iso*-propyl ether pressure–composition isotherms from 0 to 10°C have shown only the monoetherate. The pressures of dissociation and usual thermodynamic functions of dissociation and formation have been determined.[77, 78] In tetrahydrofuran, a 1 : 1 adduct is indicated from pressure–composition isotherms determined in the region −22·9 to +30°C, while a ditetrahydrofuranate is indicated from inflections in the isotherms.[318] The latter is stable below 0°C, while the former becomes predominant at 0°C and decomposes at 150°C.[596, 609] The dissociation pressures and usual thermodymanic functions of the adducts have been determined.[318] A mono-dioxanate is known[170, 532] but it is less stable than lithium tetrahydroborate: heated to 85°C, it loses both dioxane and hydrogen, in contrast to the behaviour of the other etherates which decompose to the hydroborate and ether.[170] The stabilities, based on standard free energies of dissociation, of the mono-etherates increase in the following order:

$$(iso\text{-}C_3H_7)_2O \leqslant (C_2H_5)_2O < (CH_3)_2O < (CH_2)_4O.^{77,\,78}$$

Steric factors account fairly well for the series, but heats and entropies of dissociation indicate that lattice energies and packing modes should also be considered.[77]

Pressure–composition isotherms from 0 to 80°C in the NH_3–$LiBH_4$ system show the existence of mono-, di-, tri- and tetraammoniates. A phase diagram shows that all but the triammoniate have congruent melting points.[561] Mono- and diamine adducts have been identified in the trimethylamine–lithium hydroborate system. The diamine adduct forms at -80°C, decomposes slowly at -10°C and has a vapour pressure of 84 Torr at 0°C. The monoamine adduct is prepared at 0°C, is soluble in water, slightly soluble in diethyl ether and insoluble in petroleum ether. It evolves trimethylamine at 100°C.[596] Hydrazine forms a 1 : 1 complex which melts and decomposes at 160°C.[423a]

The formation of complexes alters the solubility and reactivity of the lithium salt, exemplified by the decreased thermal stability of the dioxanate mentioned above. In ether solution, it is a more powerful reducing agent than the Na salt dissolved in water or alcohol, and the etherate does not flash in air.[427] The tetrahydrofuranate[318] and dioxanate[532] decompose more slowly in water, possibly because formation of a postulated short-lived monohydrate, $LiBH_4.H_2O$, necessary for hydrolysis, is blocked.[318] In a reaction with copper(I) chloride to produce diborane, the reaction rate increased as a function of ether concentration until a mole ratio of 1 : 1 was reached, implying enhanced reactivity of the etherate.[482]

Preparation

1. FROM DIBORANE

An alkali-metal hydroborate was first prepared[496] by use of the room-temperature reaction of ethyllithium and gaseous diborane. Side products were various ethyl derivatives of diborane:

(1) $LiC_2H_5 + B_2H_6 \rightarrow LiBH_4 +$ diborane derivatives

Possibly the most useful laboratory preparation of the lithium salt is the reaction with lithium hydride[501, 504, 173]:

(2) $2LiH + B_2H_6 \rightarrow 2LiBH_4$

The reaction proceeds only in the presence of a solvent such as diethyl ether and the product is then separated as the mono-etherate. With finely divided lithium hydride, the reaction proceeds well at atmospheric pressure and room temperature[504] while a 90% yield was reported at -50°C.[501] The ether can be removed by vacuum drying at 33°C.[613] The reaction with lithium ethoxide:

(3) $3LiOC_2H_5 + 2B_2H_6 \rightarrow 3LiBH_4 + B(OC_2H_5)_3$

is rapid and exothermic and must be cooled to prevent excessive loss of diborane. Three passes of diborane over the lithium ethoxide gave nearly quantitative conversion and 85% purity. Recrystallization from ether raised the purity to 95%.[504] Lithium methoxide reacts much more slowly. A related reaction:

(4) $3LiB(OCH_3)_4 + 2B_2H_6 \rightarrow 3LiBH_4 + 4B(OCH_3)_3$

has also been reported[504]; it is less rapid than that with the sodium salt. The reaction with lithium aluminium hydride is run at 70 to 90°C, with about 90% conversion:

(5) $LiAlH_4 + 2B_2H_6 \rightarrow LiBH_4 + Al(BH_4)_3$

It proceeds smoothly at room temperature in diethyl ether.[16]

The reaction with lithium amide proceeds smoothly, even at -64°C[480]:

(6) $B_2H_6 + LiNH_2 \rightarrow LiBH_4 + BH_2NH_2$

The conditions are analogous to those of reaction (2), a solvent, e.g. diethyl ether, being necessary to allow the reaction, which must be moderated to prevent undue hydrogen production. The product purity is about 98%, and with excess diborane the conversion of lithium amide is virtually complete.[480]

In ammonia solution, lithium reacts with the di-ammonia complex of diborane at -80°C; lithium hydroborate is removed from excess of metal by ether extraction.[478]

(7a) Reaction: $2Li + 2B_2H_6{,}2NH_3 \rightarrow 2LiB_2H_8N + H_2 + 2NH_3$

(7b) Solvent removal: $n LiB_2H_8N \xrightarrow{-NH_3} n LiBH_4 + (BH_2NH_2)n$

It is considered to be essential to remove the solvent at low temperature (−78°C) to prevent decomposition of the aminoborane to give hydrogen. The nature of the diammoniate of diborane has been shown to be that of a hydroborate.[524]

2. FROM ALKOXY-BORON COMPOUNDS

The reaction of lithium hydride with trimethoxyborane gives lithium hydroborate, although not as efficiently as the analogous Na reaction.[506] The maximum

(1) $4LiH + B(OCH_3)_3 \rightarrow LiBH_4 + 3LiOCH_3$

yield reported is 70%, compared with about 90% for the sodium hydroborate. Extraction of the crude product offers difficulty, an ether extraction giving lithium hydroborate of only 50% purity.[492] The reaction is, however, a convenient one-step laboratory process.

A reaction of the same kind between lithium aluminium hydride and alkoxyboranes is reported to give lithium hydroborate in yields of 70–90%.[312]

(2) $LiAlH_4 + B(OR)_3 \rightarrow LiBH_4 + Al(OR)_3$

3. FROM BORON HALIDES

An excess of lithium hydride in a diethyl ether solution of BF_3 etherate, heated in an autoclave at 120–130°C for several hours, gives[613] lithium hydroborate which, after crystallization from the ether, is obtained in 90% yield:

(1) $BF_3,OEt_2 + 4LiH \rightarrow 3LiF + LiBH_4$

The etherate can be decomposed by heating at 33°C under vacuum. At 25°C the system is unreactive, but the presence of a promoter (such as $LiBH_4.B_2H_6$ lithium trimethoxyhydroborate) allows $LiBH_4$ formation. The reaction can proceed further to give diborane.[171] It is suggested that the role of the promoter is to keep the lithium hydride surface free from complex lithium salts. This can also be accomplished by use of a solvent (e.g. tetrahydrofuran) in which diborane is more soluble.[138] The process patents, listed separately below, suggest other promoters. Another study of this reaction in the range −5 to +34°C indicated a maximum yield of 46% in the range 3–10°C.[169]

A two-stage reaction in ether has also been described. The first stage (combination of lithium hydride and BF_3 etherate to form diborane) is promoted by $LiBH_4$:

(2a) $6LiH + 2Et_2O.BF_3 \rightarrow B_2H_6 \uparrow + 6LiF + 2Et_2O$

The generated B_2H_6 is then passed to a second vessel containing LiH[424]:

(2b) $B_2H_6 + 2LiH \rightarrow 2LiBH_4$

A similar reaction occurs between lithium aluminium hydride and BF_3 in ether[521]:

(3) $LiAlH_4 + BF_3 \rightarrow LiBH_4 + AlF_3$

Diborane is evolved as the mole ratio $BF_3 : LiAlH_4$ approaches unity, above which diborane is produced in proportion to the excess of BF_3.

4. FROM ALKYLBORANES

A reaction reported[174] in the patent literature between triethyl borane and lithium hydride is conducted at 240°C under hydrogen pressure of 29,000 lb in^{-2}:

(1) $BEt_3 + LiH + 3H_2 \rightarrow LiBH_4 + 3C_2H_6$

5. FROM TETRAHYDROBORATES

The metathetic reaction with the sodium salt[507, 314, 502]:

(1) $LiCl + NaBH_4 \rightarrow LiBH_4 + NaCl$

is attractive because of the commercial availability of sodium hydroborate. A suitable solvent system (one in which NaCl is relatively insoluble, the reactants are soluble enough to react and $LiBH_4$ is soluble) is *iso*-propylamine.[507] The high b.p. of *iso*-propylamine is also helpful during reflux. Other effective solvents are primary amines[502], e.g. methyl- and ethylamine[507], and ammonia.[502] The crude product, refluxed and separated in ethyl ether, yields 90–95% of a 97% pure product.[507] A reaction in ethanol at −10°C gives a solution with 85–90% lithium hydroborate and 15–10% of the sodium salt. The yield is about 85%. The resulting solution, after filtration, is stable at 0°C and useful as a reducing agent.[314] The formation from lithium iodide is also described.[314] A stable solution of a dioxanate is formed with dioxan as solvent, and the solution is useful for reduction purposes.[443] Potassium hydroborate may be used with tetrahydrofuran as solvent.

The reaction between ethyllithium and aluminium hydroborate in benzene has been briefly described[509, 502]:

$$(2)\ 3LiC_2H_6 + Al(BH_4)_3 \rightarrow 3LiBH_4 + Al(C_2H_6)_3$$

6. PATENTED PROCESSES

Preparation—number	*References*
1—2	27, 364, 501
2—1	242, 360–2, 364, 450, 612
2—2	313
3—1	313
3—2	366
4—1	42, 95, 110, 262, 365, 444
5—1	174, 614
Purification	110

SODIUM TETRAHYDROBORATE

A. Structure

The nearly constant polarizability (3·94 Å) of the alkali-metal tetrahydroborates, exclusive of lithium, shows that the crystals are essentially ionic.[552] This conclusion, and the tetrahedral configuration of the hydroborate ion, are confirmed from the infra-red spectra[455], which are discussed on p. 355.

At 25°C the crystal has a cubic face-centred (NaCl) lattice with four molecules and reported cell parameters: $a = 6{\cdot}1635$[1], 6·151[538] and 6·157 at 20°C.[180] The B—Na distance (3·07 Å) and the B—B distance (4·35 Å) are sufficient to provide little hindrance to rotational displacements of the hydroborate ion.[538] Purple centres develop rapidly on exposure to X-rays fading slowly in sunlight and rapidly at 120°C.[1] At −83°C there is a λ-point[278, 554, 544] where the crystal gradually undergoes an order–disorder transition involving the orientation of the hydroborate ions.[544, 554] The disordered face-centred cubic crystal transforms into an ordered body-centred tetragonal structure.[1] The spectrum in the region 2,150–2,550 cm^{-1} confirms this change.[296] The tetragonal lattice has cell parameters: $a = 4{\cdot}354$ Å and $c = 5{\cdot}907$ Å, measured at −190°C[1], and $a = 4{\cdot}353$ Å and $c = 5{\cdot}909$ Å measured at −183°C.[180]

B. Properties

Sodium tetrahydroborate is a white crystalline solid stable to 400°C.[504] The dihydrate, formed during normal atmospheric exposure[24], has a dissociation pressure of 6·23 Torr at 25°C.[552] The anhydrous salt has a refractive index to white light of 1·54[552] and a reported density of 1·04[24] and 1·08 g cm^{-3}.[108] The crystal is ionic[552], with a m.p. near 500°C.[119, 269, 543] Thermal analysis in air shows an oxidative degradation, with weight gain beginning at 294°C. In nitrogen and hydrogen, decomposition and hydrogen evolution with weight loss begin at 503 and 512°C.[437] Another study showed melting at about 505°C and decomposition at 565°C.[543]

At 298 K, the dissociation reaction on dissolution has $\Delta H° = -776$ cal mol^{-1} measured in M NaOH[221] and $\Delta G° = -5{\cdot}660 \pm 0{\cdot}070$ kcal mol^{-1} measured in water.[552] The heat of solution measured in liquid ammonia at -33°C is $-9{\cdot}90$ kcal mol^{-1}.[24] The heat of decomposition to sodium hydride, boron and hydrogen at 250°C is $+32{\cdot}14$ kcal mol^{-1}.[529]

Heat capacities of the crystalline solid have been measured from 15–300 K[278] and from 273–673 K.[119] The second-order transition at 189·9 K has an entropy change of

Table III.—Solubility of $NaBH_4$ in Various Solvents[368a]

Solvent	Temperature (°C)	Solubility (g per 100g solvent)
Water	0	25·0
	25	55·0
	60	88·5
Liquid ammonia	−33·3	104·0
Methylamine	−20·0	27·6
Ethylamine	17	20·9
n-Propylamine	28	9·7
iso-Propylamine	28	6·0
n-Butylamine	28	4·9
Cyclohexylamine	28	1·8
Morpholine	25	1·4
	75	2·5
Aniline	75	0·6
Pyridine	5	8·1
	25	3·1
	75	3·4
Monoethanolamine	25	7·7
Dimethylformamide	25	25·5
	100	24·0
Ethylenediamine	75	22·0
Acetonitrile	28	2·0
Methanol	20	16·4 (reacts)
Ethanol	20	4·0 (reacts slowly)
iso-Propyl alcohol	25	0·37
	60	0·88
tert-Butanol	25	0·11
	60	0·18
Tetrahydrofurfuryl alcohol	20	14·0 (reacts slowly)
2-Ethylhexanol	25	0·01
Ethylene glycol monomethylether	25	16·7
Diethylene glycol monomethylether	25	16·3
Monoglyme	0	2·6
	20	0·8
Diglyme	0	1·7
	25	5·5
	45	8·0
	75	10·0
Triglyme	0	8·4
	25	8·7
	50	8·5
	100	6·7
Tetraglyme	0	8·7
	25	9·1
	50	8·4
	75	8·5
	100	4·2
Tetrahydrofuran	20	0·1
Dimethyl sulphoxide	25	5·8

1·22 cal mol^{-1} deg^{-1} and an enthalpy change of 232·6 cal mol^{-1}.[278] The usual thermodynamic functions are tabulated from 298 to 700 K,[119] and from 0 to 2000 K (for a hypothetical solid).[269] The standard thermodynamic functions at 298·16 K are[144]:

	ΔH°_f	ΔG°_f	S°	C°_p
	kcal mol^{-1}		cal mol^{-1} deg^{-1}	
$NaBH_4$	−45·65	30·22	24·26	20·72
$NaBH_4.2H_2O$	−188·23	−145·14	43·1	—
$NaBH_4$ (aq)	−46·36	−35·88	40·9	—

(standard state is M = 1)

The calculated lattice energy is 168 kcal mol^{-1}.[17]

C. Solubilities and Solvates

The solubilities of sodium tetrahydroborate in a number of solvents are given in Table III.

The solubility in pyridine has an inverse temperature dependence, with maximum solubility reported as 8·1% at 5°C.[388, 389] The general polar nature of the listed solvents follows naturally from the salt-like character of sodium hydroborate, although it is insoluble in both dioxan[506] and B_5H_9,[610] solvents whose dielectric constants are 2·2[226] and 20·8[610] at 25°C, respectively. A phase diagram for the sodium hydroborate–water system from −50 to +50°C is shown in Fig. 1. Two invariant points at −27·5°C and

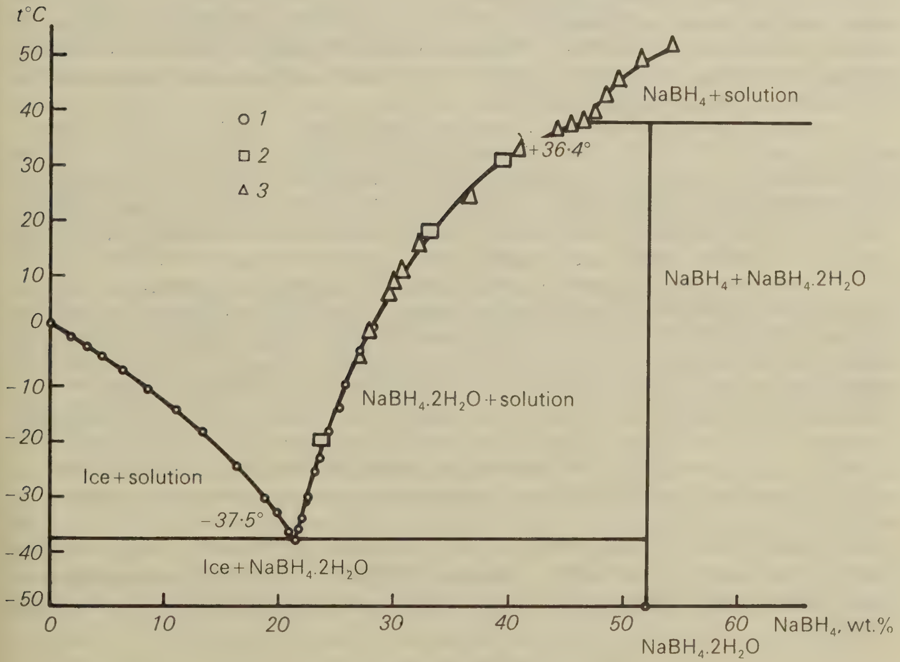


FIG. 1.—Solubility polythermal for the binary $NaBH_4$–H_2O system in 0·1 M NaOH:[383] (1) points obtained by visual observation over a range of temperatures; (2) points obtained by the isothermal method; (3) points obtained independently[276]

36·4°C are noted[371]; the latter is also given as 35 ± 1°C.[552] The region of positive slope has also been examined.[276, 368a]

The ternary system $NaBH_4$–$NaOH$–H_2O is described for 0[370, 371], 18, 30, 50[371], 25°C[337], and ternary solubility isotherms prepared.[371] Only 3 solid phases are found, namely $NaBH_4.2H_2O$, $NaBH_4$ and $NaOH.H_2O$. The purification of sodium hydroborate by recrystallization from the ternary system at 0°C has been demonstrated.[245] When sodium hydroxide is added to a saturated, i.e. 28·9%, aqueous solution of sodium hydroborate, the dihydrate is the stable solid phase until the composition is 22·3% $NaBH_4$ + 22·5% NaOH. With further quantities of sodium hydroxide, the anhydrous hydroborate is stable until the hydroborate/NaOH concentrations reach 12·3% $NaBH_4$/44·4% NaOH. Further addition again of NaOH produces $NaOH.H_2O$.

The ternary system $NaBH_4$–$NaCl$–H_2O has been studied at 0[372–3], 20[373] and 25°C.[337] The solid phases are $NaBH_4.2H_2O$ $(NaCl/NaBH_4)\ 2H_2O$ and NaCl. One study[373] can be adequately described as an approach to one side of the quaternary system $NaOH$–$NaBH_4$–$NaCl$–H_2O, since a concentration of 1% NaOH is used throughout. The major portion of the 3-system diagram has NaCl as the solid phase, indicating that $NaBH_4$ is salting out NaCl.[372] In the analogous NaBr ternary system, only one solid solution, of varying $NaBH_4$/NaBr ratio, is observed at 0°C[372], and at 0 and 20°C with 1% NaOH.[374]

The quaternary system $NaOH$–$NaBH_4$–$NaCl$–H_2O at 25°C has been studied to define regions which have the species $NaOH.H_2O$, NaCl and $NaBH_4.2H_2O$ in the solid phase. In addition, a fourth field must correspond to a solid solution of NaCl and $NaBH_4$. The diagram suggests the possibility of removing most of the NaCl present in an alkaline sodium hydroborate solution.[337]

The increased solubility of diborane in a solution of diglyme and sodium hydroborate with increasing hydroborate concentration implies the presence of an etherate–hydroborate complex[620] and a 1 : 1 NaOH–diglyme adduct has been reported.[57] Studies of the $NaBH_4$–$HCONMe_2$ system have shown 4 solid phases, viz. $NaBH_4$, $NaBH_4.HCONMe_2$, $NaBH_4.2HCONMe_2$ and $NaBH_4.4HCONMe_2$,[376–7] with transition points, in contact with solution, at 26·5, 20·5 and 8·7°C. A $3HCONMe_2$ species is reported to have a m.p. of 29°C.[568] Studies on the $Mg(BH_4)_2$–$NaBH_4$–$HCONMe_2$ system have shown, in addition to the 2- and 4-$NaBH_4$ adducts, the presence of the $6HCONMe_2$ adduct of $Mg(BH_4)_2$.[319]

In ammonia, several solvates have been reported: mono-,[7] di-,[504] tri-,[131, 133] tetra-[7] and 4·5 species.[132, 133, 131] The di-ammoniate was found after evaporation of an ammonia solution of sodium hydroborate, and was categorized as unstable. Investigations of the $NaBH_4$–NH_3 systems from −100 to 0°C[132], −49·8 to +25°C[133] and −28 to +95°C[131] (with pressure up to 20 atm.) have indicated the existence only of the compounds, $NaBH_4.3NH_3$ and $2NaBH_4.9NH_3$, which melt at −16·0 and −20·5° C[133, 132], respectively. The partial molar heats and entropies of ammonia, and the integral heats of solutions of sodium hydroborate in ammonia have been calculated for the range 40 to 50°C.[131] A study of the system $NaBH_4$–N_2H_4, using 0 to 85·5 wt.-% $NaBH_4$, in the range −120 to +80°C, indicates the existence of four compounds: $NaBH_4.2N_2H_4$ (m.p. 53°C), $2NaBH_4N_2H_4$, $NaBH.N_2H_4$ and $NaBH_4.6N_2H_4$.[130]

Solvates containing 2·5 and 3·0 pyridine molecules per molecule of $NaBH_4$ have been observed.[388, 389] The higher solvate is converted to the lower at −4·7°C, and the lower to sodium hydroborate at 5°C.[389] Both are unstable in a vacuum. Acetamide forms an addition compound, m.p. 100°C, and triethylenetetramine forms a white solid m.p. 85°C.[568]

The binary system $NaBH_4$–NaH shows a eutectic at 395–400°C and 79 wt.-% $NaBH_4$. Decomposition of $NaBH_4$ occurs at 595–600°C, a temperature significantly higher than the 565°C reported for the pure phase. A binary phase diagram has been prepared.[543]

D. Preparation

1. FROM DIBORANE

Sodium hydroborate was probably first prepared by Stock *et al.*[550], although they assigned an empirical formula, $Na_2B_2H_6$ disodium diborane, to the solid product. The reaction has been repeated by shaking sodium amalgam with diborane under pressure: several days were allowed for completion of the reaction. More B_2H_6 was absorbed than is called for by formation of disodium diborane.[294] The reaction has been run in ethyl and *n*-butyl ether, the former being preferable, and is more rapid than Stock's method, being completed in two days.

(1) $2NaH + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8$

A yield of 80% is based upon the more easily isolated product, NaB_3H_8. Intermediates, of composition $Na_2B_2H_6$ and NaB_2H_6, have been postulated: evidence for the former was obtained by extracting an incomplete reaction mixture to give a material whose X-ray diffraction pattern could be ascribed to $Na_2B_2H_6$, and which disappears on standing, to be replaced by the pattern of $NaBH_4$.[256]

Although the reaction between lithium hydride and diborane proceeds smoothly, that with sodium hydride does not[504]: the reaction proceeds:

(2) $2NaH + B_2H_6 \xrightarrow{\text{solvent}} 2NaBH_4$

at room temperature only in the presence of a solvent (for the $NaBH_4$)[62], e.g. diglyme[62] and tetrahydrofuran.[424] Addition of diborane above the mole ratio $B_2H_6 : NaBH_4 = 0{\cdot}5$ in diglyme causes additional diborane absorption, apparently in accordance with the equation[62]:

(3a) $2NaBH_4 + B_2H_6 \rightarrow 2NaBH_4,BH_3$

Passing even a dilute stream of diborane gas over solid sodium trimethoxyhydroborate removes diborane almost completely. If the reaction is written to include preparation of the trimethoxyhydroborate[504, 502, 60], a net reaction equivalent

(3b) $2NaH + 2B(OCH_3)_3 \rightarrow 2NaBH(OCH_3)_3$

(3c) $2NaBH(OCH_3)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$

to equation (2) is obtained. Any dimethoxyborane present in the diborane will also react with the trimethoxyhydroborate to form $NaBH_4$[504]:

(3d) $3(CH_3O)_2BH + NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3B(OCH_3)_3$

A description of a general reaction between trialkylamine boranes and NaH to produce $NaBH_4$ has been given.[308] The reaction proceeds at 100 to 300°C:

(4) $NaH + H_3B,NR_3 \rightarrow NaBH_4 + NR_3$; R = alkyl

A reaction between the diammoniate of diborane, demonstrated to be a tetrahydroborate[524] $[H_2B(NH_3)_2][BH_4]$, and sodium in liquid ammonia gives sodium hydroborate after solvent removal and ether extraction of the solid residue at low temperature.[478]

(5) $2Na + 2[H_2B(NH_3)_2][BH_4] \xrightarrow{NH_3} 2NaBH_4 + H_2 + 2NH_3 + 2BH_2NH_2$

A patent[346] describes a similar preparation from solid boron hydride polymers, NaH and H_2 at 800 lb in^{-2}. The solvent is a glyme: the reactor is heated to 50°C for 94 h.

A compound originally described[550] as a 'sodium hypoborate' produced from diborane and aqueous sodium hydroxide has been shown to be sodium hydroborate formed in the reaction[105]:

(6) $4NaOH + 2B_2H_6 \rightarrow 3NaBH_4 + NaB(OH)_4$

A rapid, exothermic reaction between diborane and sodium methoxide freshly prepared from the thermal decomposition of Na tetramethoxyborate gives $NaBH_4$ of 96% purity: no solvent is required[504, 502]:

(7) $3NaOCH_3 + 2B_2H_6 \rightarrow 3NaBH_4 + B(OCH_3)_3$

Sodium tetramethoxyborate also reacts directly with diborane at −80°C with no solvent.[504, 502] Reactions (7) and (8) are similar to (3b, c) but require more diborane. Together they comprise the first reported syntheses of $NaBH_4$:

(8) $2B_2H_6 + 3NaB(OCH_3)_4 \rightarrow 3NaBH_4 + 4B(OCH_3)_3$

A patent describes the reaction between metal alkoxides (e.g. CH_3ONa) and alkyl diboranes (e.g. $B_2H_2(n\text{-}C_3H_7)_4$); heating to distil off volatile products left $NaBH_4$.[555]

2. FROM ALKOXY-BORON COMPOUNDS

A mixture of NaH and a trialkoxyborane will react according to equation (1) at about 250°C.[502, 506] The product can be extracted by a solvent in which it is soluble to the exclusion of sodium alkoxide, such as liquid ammonia and *iso*-propylamine.[502] The yields of the reaction and extractions are 90–96% with purities of 90–96% in both these cases.[506] When R is methyl and with some grades of NaH, a side reaction produces sodium trimethoxyhydroborate. This difficulty is avoided if R is ethyl or *n*-propyl: if ethyl, however, the reaction temperature must be carefully controlled, as sodium ethoxide decomposes above 240°C.[506] The process is extensively noted in the patent literature. A similar reaction between Na, H and alkoxy boranes under pressure at 250°C gave low yields in the absence of good agitation.[506]

(1) $4NaH + B(OR)_3 \rightarrow NaBH_4 + 3NaOR; \quad R = \text{alkyl}$

Sodium trimethoxyhydroborate, found as an impurity in the preceding reaction, is extractable in tetrahydrofuran or diglyme, where it undergoes a rapid decomposition at low temperatures (65–70°C) to form $NaBH_4$.[58]

(2a) $NaH + B(OCH_3)_3 \rightarrow NaBH(OCH_3)_3$

(2b) $4NaBH(OCH_3)_3 \xrightarrow{\text{solvent}} NaBH_4 + 3NaB(OCH_3)_4$

In diglyme, sodium hydroborate is soluble and sodium tetramethoxyborate insoluble. In tetrahydrofuran these solublities are reversed.[58]

Reduction of sodium tetramethoxyborate by-product (equation 2b) in diglyme, using aluminium and hydrogen at 2,000 lb in^{-2} and 180°C, has been reported[15]:

(3) $3NaB(OCH_3)_4 + 4Al + 6H_2 \rightarrow 3NaBH_4 + 4Al(OCH_3)_3$

The patent literature suggests other methods for the improvement of reaction (1). Reaction with silane[128] or alkylsilanes[291] provides a means for converting sodium tetramethoxyborate at below 100°C.[128]

(4) $NaB(OCH_3)_4 + SiH_4 \rightarrow NaBH_4 + Si(OCH_3)_4$

A reaction with CO_2 in tetrahydrofuran provides an effective means of recycling the tetramethoxyborate, and the resulting trimethoxyborane can then be reacted as in equation (1)[325]:

(5) $NaB(OCH_3)_4 + CO_2 \xrightarrow{\text{THF}} NaCH_3,CO_3 + B(OCH_3)_3$

The patent literature mentions extensively the purification of $NaBH_4$ as produced in reaction (1). Dissolving the reaction products in water[574, 412, 214, 581] decomposes excess sodium hydride and allows the methanol-promoted recrystallization of sodium hydroborate.[39] If the reaction is run in mineral oil, extraction by ammonia[38] or amine[168, 611, 197, 531] will remove the oil and the hydroborate: the latter is isolated by recrystallization. Other schemes using water and ammonium chloride[213], diglyme[113], glymes in general[490] and *iso*-butanol[40] have been mentioned.

3. FROM BORON HALIDES

The addition of BF_3 to NaH in diethyl ether produces an addition product stable to about 200°C[207]

(1a) $NaH + BF_3 \rightarrow NaHBF_3$

The technology of this method is an attempt to promote continued reaction with sodium hydride. The overall reaction is much more sluggish than the corresponding lithium reaction, possibly because of the greater solubility of lithium tetrahydroborate.[505]

(1b) $NaHBF_3 + 3NaH \rightarrow NaBH_4 + 3NaF$

In the presence of a more suitable solvent for the sodium salt, tetrahydrofuran or diglyme, side reactions destroy the efficiency[62]:

(1c) $6NaH + 8BF_3 \rightarrow 6NaBF_4 + B_2H_6$

(1d) $7NaH + 8BF_3 \rightarrow 6NaBF_4 + NaBH_4BH_3$

As with the lithium reaction, promoters are suggested in the patent literature for carrying out the complete reaction:

(1e) $4NaH + BF_3 \rightarrow NaBH_4 + 3NaF$

Specific promoters described are: alkyl borates[111], diethlamino boranes[156], boron alkyls[157, 287–9], alkyl halides[157, 288], primary and secondary amines[156] and sodium alkoxide.[459] Reported yields in the 90% range are not uncommon. The purpose of the promoter appears to be solubilizing the NaH, often as an addition product, to the extent that hydroborate is not formed at the surface of the solid NaH where it can inhibit further reaction. An alternative approach involving ball milling has also been described.[508] The reaction between NaH and BCl_3 proceeds at 80°C in the presence of triethylaluminium.[621]

The similar reaction between Na, H_2 and boron trifluoride is also discussed in the patent literature. It is operated at 50–75 lb in^{-2} and

(2) $4Na + 2H_2 + BF_3 \rightarrow NaBH_4 + 3NaF$

200°C[266], at 200–300°C with sodium dispersed over sodium chloride[450], and with sodium dispersed in an inert liquid at 250–350°C.[489]

A reaction between Na, H_2 and sodium tetrafluoborate is also patented with amines and glymes as solvents, and without solvent[489]:

(3) $NaBF_4 + 4Na + 2H_2 \rightarrow NaBH_4 + 4NaF$

A patent describes the reaction between NaH and BCl_3 in diglyme at 150°C.

(4) $4NaH + Me_3N,BCl_3 \rightarrow Me_3N + 3NaCl + NaBH_4$

Lower tertiary aliphatic amine solvents are also suggested.[47]

4. FROM BORATES

Because of the wide availability of borates of high purity and their relatively low cost, their direct reduction to sodium hydroborate is discussed widely in the patent literature. The success of the methods seems to have been somewhat less than total.

The simplest reaction is between NaH and boric oxide, at 200–275°C

(1) $4NaH + 2B_2O_3 \rightarrow NaBH_4 + 3NaBO_2$

and under pressure.[500] Sodium alkoxides are claimed to be catalysts.[460] The presence of silica further promotes the reaction.[162] Generation of NaH *in situ* is also mentioned.[492]

A direct reaction between a sodium borate glass, i.e. anhydrous borax $Na_2O.2B_2O_3$, and sodium and hydrogen is described[512]; the borax and silica

(2) $Na_2O.2B_2O_3 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$

are fused at 500°C and react with sodium and hydrogen at 3 atm. The reaction is covered in the patent literature for many metal borates, calcium hydride or aluminium and silica. The general reaction, using an arbitrary divalent metal

(3) $MO.B_2O_3 + SiO_2 + 2Na + 2H_2 \rightarrow 2NaBH_4 + MSiO_3$

metaborate and silica, gives the desired $NaBH_4$ and the metal silicate. The addition of

Table IV.—Production of $NaBH_4$ from Borates

Borate	'Free energy agent'	Reducing agent	Reference
$Na_2B_4O_7$	SiO_2	Na + H	163, 149, 167
$Na_2B_4O_7$	Al, Mg	NaH	535
$NaBO_2$		CaH_2	145
$NaBO_2$		Al + H	147
MgB_4O_7	SiO_2	Na + H	163
Na_3BO_3	Si	Si + Na + H	202
$NaCaB_5O_9$	Al	Al + Na + H	167
$Ca_2B_6O_{11}$	Al	Al + Na + H	167

silica and formation of a metal silicate in place of the oxide greatly increase the change in free energy and, presumably, enhance the rate and degree of completeness of the reaction.

A list of patents covering procedures generally following the scheme of reactions (2) and (3) is given in Table IV.

Refluxing boron phosphate in mineral oil at 300°C with sodium hydride has also been patented[46]: a yield of about 5% was achieved.

(4) $BPO_4 + 4NaH \rightarrow NaBH_4 + Na_3PO_4$

5. PATENTED PROCESSES

Preparation—number	*References*
1—1	558, 220
1—2	432, 582, 274, 331, 87, 421
1—3	497
1—4	557, 559, 497, 556, 307
1—6	346
1—8	498, 499
1—9	555
2—1 (Preparation)	270 212, 31, 260, 449, 31, 25, 59
2—1 (Purification)	213, 214, 412, 168, 113, 490, 581, 40, 611, 38, 574, 197, 531, 27, 37
2—4	291, 128
2—5	325
3—1	150, 513, 290, 112, 488, 287, 227, 515, 288, 157, 156, 111, 83, 289, 459, 489, 266
3—2	489, 266
3—4	47, 275, 515
4—1	162, 460, 461
4—2	514
4—3	45, 166, 159, 153, 105, 115, 143, 310, 311, 205–6, 116–167, 202, 147, 145, 149, 163
4—4	46

POTASSIUM TETRAHYDROBORATE

A. Structure

Neutron diffraction of potassium hydroborate shows a tetrahedral array of hydrogen atoms about the boron atom, with a B—H distance of 1·219 Å.[448] Polarizability studies of the alkali-metal hydroborates indicate that the potassium salt is essentially ionic, as are all but lithium.[552] At room temperature, the crystal is face-centred cubic with reported lattice parameters: $a = 6{\cdot}7272$ Å at 26°C[1] and 6·722 Å at 20°C.[180] Faint blue colour-centres develop on exposure to X-rays.[1]

A second-order transition has been observed at −197·3°C[522, 544] and −196·8°C[188], corresponding to an order–disorder transition of the hydroborate ion. Below this point, unlike that of the sodium salt, the potassium hydroborate crystal structure is still face-centred cubic. The lattice parameter, a, is reported to be 6·636 Å at 90 K.[180]

B. Properties

Crystalline potassium hydroborate is ionic[552], has a m.p. at about 585°C[384] as measured during differential thermal analysis, a density of 1·11 g cm^{-3} [24] and a refractive index of 1·490[24] and 1·494[552] in white light at 25°C. The salt is stable to hydrolysis on exposure to a normal atmosphere[24], while the Na analogue is not. The tri- and monohydrates as well as the anhydrous salt have been isolated. Transitions between the respective forms occur, in contact with saturated solutions, at 7·3 and 37·5°C.[383] The compound is stable to about 500°C,[24] and its thermal response has been studied.[437, 384]

When heated, presumably in an inert atmosphere, the compound exhibits 3 endothermic effects: the first, at 590°C, occurs at fusion and is reversible; the second, at 640°C, indicates the onset of measurable hydrogen evolution, which continues to 695°C where (the third effect) the decomposition becomes vigorous.[384] Heating in air causes an oxidative weight gain at 480°C; heating under hydrogen retards detectable hydrogen evolution up to 626°C.[437] At 76 K the salt undergoes a second-order transition, coinciding with a λ point in the heat capacity measurements.[544] The enthalpy of the transformation is 58·4 cal mol^{-1} and the entropy is 0·77 e.u.[522] The heat of solution in liquid nitrogen at -33°C is $-1{\cdot}33$ kcal mol^{-1},[92] and in water at 25°C is $-84{\cdot}62$ kcal mol^{-1}.[277] The heat of decomposition at 25°C into B and H_2 is $+40{\cdot}88$ kcal mol^{-1}.[529]

The heat capacity of the crystalline solid has been measured from 15 to 375 K[188] and from 273 to 673 K.[119] The enthalpy[277] and free energy[92] of formation have been calculated. The usual thermodynamic functions have been tabulated from 25 to 300 K[186], from 298 to 700 K[119], and from 0 to 2000 K[269] for a hypothetical solid. At 298·16 K:

	Reference
$\Delta H^\circ_f = 55{\cdot}42$ kcal mol^{-1}	144
$\Delta G^\circ_f = 39{\cdot}82$ kcal mol^{-1}	144
$S^\circ = 26{\cdot}7$ cal deg^{-1} mol^{-1}	144
C_p (298·15) $= 23{\cdot}081$ cal deg^{-1} mol^{-1}	119

The lattice energy has been calculated as 159 kcal mol^{-1}.[17]

C. Solubilities and Solvates

The solubilities of potassium hydroborate in a number of solvents are given in Table IV. Generally, ethers and hydrocarbons are poor solvents: moreover, the potassium salt is usually less soluble than the sodium salt. The phase diagram of the system KBH_4–H_2O up to 40% KBH_4 is shown in Fig. 2, which indicates three states of

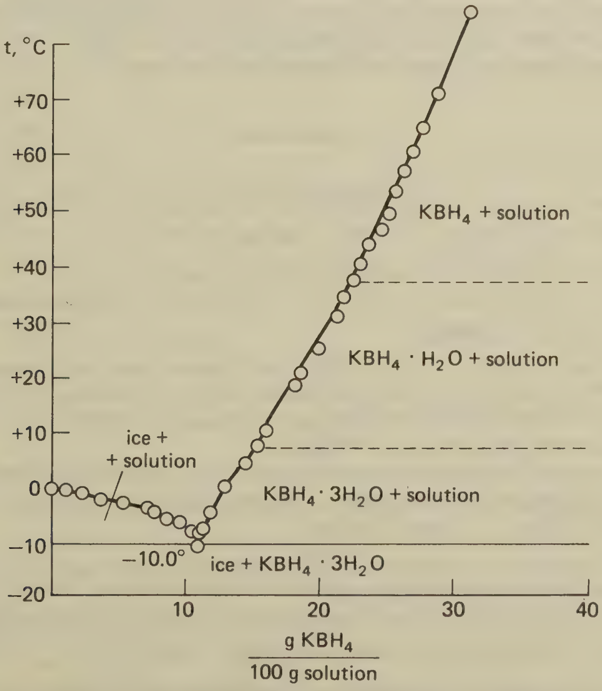


FIG. 2.—Equilibrium diagram of the KBH_4–H_2O system[383]

hydration, viz. 0, 1 and 3 molecules of hydration, all stable in contact with saturated solution. The isolated hydrates are unstable and can readily be converted to the anhydrous form at −5 to 10°C *in vacuo*.[383]

Fusion diagrams for the system $KOH–KBH_4$ show a eutectic at 5·3% KBH_4 and 347°C. Reaction between the components takes place to a certain extent above about 400°C.[384–5]

$$KBH_4 + KOH \rightarrow KBH_3OH + KH$$

Table V.—Solubility of KBH_4 in Various Solvents

Solvent	Temperature (°C)	Solubility g per 100g solvent
Water	25	19·0
Liquid ammonia	−33·3	20·0
n-Butylamine	28	0·08
Dimethylformamide	25	15·0
Ethylenediamine	75	3·9
Acetonitrile	28	0·29
Methanol	20	0·7
Ethylene glycol monomethylether	25	0·0
Diethylene glycol monomethylether	25	0·0
Monoglyme	0	0·0
	20	0·0
Diglyme	0	0·0
	25	0·0
Triglyme	0	0·1
	25	0·1
Tetraglyme	0	0·0
	25	0·0

Solubility isotherms for the ternary system $KBH_4–KOH–H_2O$ at O and 20°C show with increasing KOH concentration a smooth decrease in KBH_4 solubility. The stable solid hydroborate species are the tri-, mono- and zero-hydrates, while the possible existence of unstable octa-, tetra- and di-hydrates is indicated.[383]

D. Preparation

1. FROM DIBORANE

The first reported preparation of KBH_4 was by reaction (1). This reaction proceeds

(1) $3KB(OCH_3)_4 + 2B_2H_6 \rightarrow 3KBH_4 + 4B(OCH_3)_3$

rapidly at −80°C, the diborane reacting almost completely.[504, 502]

The reaction between diborane and KH, attempted within the range −185 to

(2) $2KH + B_2H_6 \rightarrow 2KBH_4$

+200°C, was not successful up to 180°C and above that temperature diborane decomposed.[208] The use of a solvent, particularly diglyme, is claimed in a patent[87] to dissolve the hydroborate and allow reaction to proceed. This behaviour is similar to that exhibited by the analogous sodium system.

A reaction between KOH solution and diborane at 0°C has been described[492, 387] and is analogous to the original[550] preparation of the sodium salt:

(3) $3KOH + 2B_2H_6 \rightarrow 3KBH_4 + B(OH)_3$

No reaction between potassium methoxide and diborane took place at room temperature, in contrast to the sodium analogue.[504]

Diborane and potassium aminotrimethylborane react in ether to give a product

(4) $B_2H_6 + K[H_2N,BMe_3] \rightarrow KBH_4 + H_2NBH_2 + BMe_3$

described as an equimolecular mixture of polymeric aminoborane and potassium hydroborate.[250] The reaction does not proceed in the absence of solvent.

'Yellow solids', a residue from the pyrolysis of diborane, are claimed, in a patent, to react with a solution of potassium hydroxide.[89] After centrifuging and evaporation, the aqueous residue is treated with liquid ammonia. Potassium hydroborate of 70% purity is recovered after evaporation of the ammonia.

2. METATHESIS

Because of the relative ease of preparation and the commercial availability of sodium tetrahydroborate, metathesis provides possibly the cheapest and easiest route to the potassium salt.

A commercial process[172] reacts potassium hydroxide with sodium hydroborate

$$(1)\ NaBH_4 + KOH \rightarrow NaOH + KBH_4$$

(prepared from NaOH and trimethoxyborane in oil). Water is added, the oil and water phases are separated, and KOH is added to precipitate KBH_4. In the laboratory, an aqueous solution can be simply filtered and the residue washed with ethanol.[24]

The use of a solvent in which sodium hydroborate, the reaction products of its preparative reaction, and NaOH are soluble, and in which KBH_4 is insoluble, is described in several patents. Methanol, ethanol, *iso*-propylamine[26, 41], aqueous NaOH or KOH, and butylamine[97] have been suggested.

Patents describe other potassium salts which will react with $NaBH_4$ as in reaction (1). Mentioned are potassium thiocyanate[26, 98], potassium iodide and bromide[26], and potassium acetate.[41, 26] A patented variant of reaction (1) is a two-stage metathesis in which addition of methylammonium chloride forms the ammonium tetrahydroborate which, when treated with potassium metal, gives KBH_4.[32] Another calls for direct treatment of the sodium salt with potassium amalgam in butylamine.[99]

3. MISCELLANEOUS PREPARATIVE REACTIONS

Hydrolysis of magnesium boride in aqueous KOH at room temperature gives quite pure KBH_4, according to equation (1)[299]:

$$(1)\ MgB_2 + 2KOH + 2H_2O \rightarrow KBH_4 + KBO_2 + Mg(OH)_2$$

Direct reduction of boric oxide by potassium and hydrogen has been accomplished in a ball mill at 350°C[81]:

$$(2)\ 8K + 4H_2 + B_2O_3 \rightarrow 3K_2O + 2KBH_4$$

Potassium hydroborate was obtained in 90% yield and low purity from the reaction of KH and BCl_3 in the presence of triethylaluminium[621]

$$(3)\ 4KH + BCl_3 \xrightarrow{AlEt_3} KBH_4 + 3KCl$$

4. PATENTED PROCESSES

Preparation—number	*References*
1—2	87
1—5	89
2—1	25, 97, 96, 26, 98, 99, 533, 32
3—1	300

RUBIDIUM AND CAESIUM TETRAHYDROBORATES

A. Structure

Both caesium and rubidium tetrahydroborates in their crystalline states are essentially ionic.[552] Both have the face-centred cubic lattice characteristic of the alkali-metal tetrahydroborates (excluding that of lithium), with measured lattice constants $a = 7{\cdot}029$ Å for Rb and 7·419 Å for Cs, both at 25°C.[1] Another report gives the values as Rb 7·23 Å and Cs 7·48 Å: no temperature is mentioned.[369] The salts undergo an order–disorder transition: Rb at −229°C and Cs at −246°C.[544]

B. Properties

Rubidium and caesium tetrahydroborates are white, stable, crystalline[369], non-hygroscopic salts[24] of essentially ionic character.[552, 369] Heated in air they burn at 320–350°C.[369] The several reported values for some of their physical constants are listed in Table VI.

Table VI.—Density and Refractive Index of Rubidium and Caesium Tetrahydroborate

	Density (g cm^{-3}) at 25°C	Refractive index at 25°C
$RbBH_4$	1·771[369], 1·71[24],(a) 1·711[369](b)	1·483[552],(c) 1·487[24], 1·483[369]
$CsBH_4$	3·61[369], 2·11[24],(a) 2·419[369](b)	1·496[552],(c) 1·498[24], 1·495[369]

(a) X-ray
(b) Direct measurement
(c) White light

Both compounds are stable to 600°C in an inert atmosphere; rapid decomposition starts at 650°C for the Rb salt and occurs in the region 660–700°C with the Cs salt. Under vacuum, the initial decomposition is depressed to 560°C for $RbBH_4$ and to 570°C for Cs hydroborate.[369] The apparent occurrence of polymorphism has been noted at 450°C in the Cs salt.[369] Rb and Cs hydroborates have second-order, order–disorder transitions at 44 ± 3 K and 27 ± 1 K, respectively.[544] The following thermodynamic functions have been calculated, presumably for 25°C[369]:

	Rubidium	*Caesium*
ΔH°_f	$-59{\cdot}0$ kcal mol^{-1}	$-53{\cdot}0$ kcal mol^{-1}
ΔG°_f	$-43{\cdot}0$ kcal mol^{-1}	$-16{\cdot}0$ kcal mol^{-1}
S°	28·9 cal mol^{-1} deg^{-1}	32·0 cal mol^{-1} deg^{-1}
Lattice Energy	155 kcal mol^{-1}	150·6 kcal mol^{-1}

The standard entropy of $CsBH_4$ has also been calculated as 30·5 cal mol^{-1} deg^{-1} at 25°C.[293] The heat of solution of $RbBH_4$ in liquid ammonia at -33°C is $-0{\cdot}6$ kcal mol^{-1} and ΔH°_f at 298 K is calculated to be $-56{\cdot}6$ kcal mol^{-1}.[92]

Saturated solutions in methanol at 26°C of Rb and Cs hydroborates contain 6·1 and 14·2 wt.-%, respectively.[369]

C. Preparation

Rubidium and caesium hydroborates can be prepared from a nearly saturated methanolic solution of the metal methoxide to which is added $NaBH_4$. The solid

$$(1)\quad MOCH_3 + NaBH_4 \rightarrow MBH_4 + NaOCH_3; \quad M = Rb, Cs$$

reaction product is filtered, washed with methanol and dried. Yields of 95% and 85% were obtained[24] for the Rb and Cs salts, respectively. An issued patent[41] describes the process. Rb and Cs hydroborates may also be prepared metathetically from their hydroxides in aqueous or alcoholic solutions.[369]

REACTIONS OF ALKALI-METAL TETRAHYDROBORATES

The reactions are listed by chemical groups. The appropriate group is determined, rather arbitrarily, by the principal characterizing element, or group, in the non-hydroborate molecule.

Group IA

HYDROGEN

The reversible thermal decomposition of lithium hydroborate with the evolution of hydrogen[496] can be retarded in a hydrogen atmosphere.[437] Deuterated Li, Na[73] and K[359] hydroborates can be prepared by exchange at 200, 350 and 500°C, respectively. Studies of the potassium reaction indicate[359] that both exchange and pyrolysis proceed via the reaction: $2BH_4^- \rightarrow 2H^- + B_2H_6$. Other reactions of alkali-metal hydroborates with Group IA compounds are of the metathetical class covered in the sections on preparation.

Group IB

The reduction, in diethyl ether, of $CuCl_2$ by $LiBH_4$ at -45°C gives $CuBH_4$, LiCl, B_2H_6 and H_2. At -12°C, $CuBH_4$ decomposes to give Cu, B_2H_6 and H_2, while at ambient temperatures the catalytic decomposition of B_2H_6 produces more hydrogen.[304] In aqueous solution, Cu(II) is reduced by $NaBH_4$ to almost pure copper, contaminated only by small amounts of other copper species. Silver is precipitated as Ag_2O at pH 11, while gold compounds form a precipitate which turns golden on ignition. The coinage metals cannot be separated by aqueous hydroborate reduction.[247] Aqueous $CuSO_4$ at O°C is reduced by $NaBH_4$ to a Cu–CuH mixture containing 30% CuH.[380] Complexes of Cu(I) and tertiary phosphines (L) react with $NaBH_4$ in $CHCl_3$ to give compounds of the form L_2CuBH_4.[82] Similar silver complexes are formed in pyridine.[44]

Group IIA

The reactions of alkali-metal hydroborates with compounds of Group IIA metals are generally metathetic producing the corresponding alkaline-earth hydroborate. The reaction $MgCl_2 + 2NaBH_4 \rightarrow Mg(BH_4)_2 + 2NaCl$ proceeds to about 90% completion at 25–50°C in dimethylformamide. Adding diethyl ether, benzene or diglyme at -7 to -5°C precipitates the complexes, in this instance as $Mg(BH_4)_2.6DMF$.[378] The reactions in absolute alcohol at -50°C[314] and -60°C[316] have also been described. A reaction between $NaBH_4$ and magnesium bromide takes a different path: in diethyl ether at 90Mg/10B alloy is formed, but the formation of thick deposits was not attained.[90]

The metathetic reaction to form calcium hydroborate has been carried out in ethanol at -35°C[315] and -50°C[314], in dimethylformamide at 25°C, and in pyridine with distillation of excess solvent.[569] The formation of Sr and Ba hydroborates by metathesis has been effected in ethanol at -25°C and in dimethylformamide at $+25$°C.[94, 315]

Group IIB

Compounds of this group react by reduction, although the formation of hydroborates may be intermediate stages of the overall reaction. The conversion of zinc in aqueous solution proceeds through the hydroborate to the hydroxide, while that of cadmium and mercury proceeds to the metal.[485, 394] The mechanisms postulated for cadmium entail the existence in sequence of Cd^{2+}, $Cd(BH_4)_2$, CdH_2 and Cd, while an analogous sequence for Zn has, as the last step, the decomposition of ZnH_2 to $Zn(OH)_2$.[394]

Group IIIB

1. BORON COMPOUNDS

(a) *Boron Hydrides*

Sodium hydroborate and diborane react at or near room temperature in ether solution to give [124] the B—H—B bridged diborane $(7)^{-1}$ ion[363, 20, 61, 21]:

(1) $2NaBH_4 + B_2H_6 \rightarrow 2NaB_2H_7$

At 100°C in ether solution, the reaction proceeds to the triborane $(8)^{-1}$ ion[190, 390]:

(2) $NaBH_4 + B_2H_6 \rightarrow NaB_3H_8 + H_2$

The B_2H_6 for this reaction can be prepared *in situ* by using a deficiency of BF_3 etherate, giving an overall reaction[190]:

(3) $4BF_3,Et_2O + 5NaBH_4 \rightarrow 3NaBF_4 + 2NaB_3H_8 + 2H_2 + 4Et_2O$

At high temperatures (> 50°C) the reaction between diborane and $NaBH_4$ can take different courses, depending upon reaction conditions. At temperatures just above 50°C, and in ether solvents, the reaction products are $NaB_{11}H_{14}$ and $Na_2B_{12}H_{12}$ in a ratio dependent upon reaction conditions.[390] For example, in dimethoxyethane at 120°C, the respective relative amounts are 40:50, while in dioxan at 120°C only $NaB_{11}H_{14}$ is found.[390–1] $NaBH_4$ and B_2H_6 in triethylamine react nearly quantitatively in the range 100–180°C accordingly to the equation[390]:

(4) $2NaBH_4 + 5B_2H_6 \rightarrow Na_2B_{12}H_{12} + 13H_2$

The process has been patented for 120°C in triethylamine[392] and 100°C in 1:2-dimethoxyethane.[126] Reaction at 162°C in diglyme forms a completely different borane anion, $B_6H_6^-$, in about 10% yield.[36] Sodium tetradeuteroborate reacts with B_4H_{10} in diglyme at −45°C

(5a) $B_4H_{10} + NaBD_4 \rightarrow B_2H_3D_3 + NaB_3H_7D$.

The suggested reaction mechanism involves[440]:

(5b) $B_4H_{10} \rightarrow B_3H_7 + BH_3$

(5c) $BD_4^- + B_3H_7 \rightarrow B_3H_7D^- + BD_3$

(5d) $BD_3 + BH_3 \rightarrow B_2D_3H_3$

A reaction for the preparation of sodium triborane (8) has been patented[129]:

(6a) $2NaBH_4 + 2B_3H_7{,}L \rightarrow 2NaB_3H_8 + 2L + B_2H_6$

where L = ether, thioether, amine or phosphine: the adducts can be obtained directly by the reaction:

(6b) $2B_4H_{10} + 2L \rightarrow 2B_3H_7{,}L + B_2H_6$

as suggested by equations (5) above. The reaction with decaborane (14) in ether at 25°C is a two-stage process involving the $B_{10}H_{15}^-$ and $B_{10}H_{13}^-$ ions[487]:

(7a) $2NaBH_4 + 2B_{10}H_{14} \rightarrow 2NaB_{10}H_{15} + B_2H_6$

(7b) $NaB_{10}H_{15} \rightarrow NaB_{10}H_{13} + H_2$

The first stage may also be run in diglyme, or with $LiBH_4$ in ether.[487, 255] At 90°C in dioxan, Li and Na borohydrates react differently, allowing insertion of a B atom, to give the $B_{11}H_{14}^-$ ion[8]:

(8) $NaBH_4 + B_{10}H_{14} \rightarrow NaB_{11}H_{14} + 2H_2$

The borane product may be isolated as $2NaB_{11}H_{14}.5C_5H_{10}O$ or, in the reaction with $LiBH_4$, $LiB_{11}H_{14}.2C_5H_{10}O$. Non-solvated caesium salts have been isolated.[8] The reaction proceeds at reflex in diglyme to give $NaB_{11}H_{14}$, diglyme.[6]

In aqueous solution, the addition of KBH_4 and CsCl (or RbCl) to $B_{10}H_{14}$ results in the formation of the salt $Cs_2B_{10}H_{14}{,}CsCl$ (or $Rb_2B_{10}H_{14}{,}RbCl$).[415] Salts of the type $Cs_2B_{12}H_{12}{,}CsY$ (where Y = Cl, CN, BH_4) have been isolated.[416]

(b) *Boron Halides*

The reaction between boron trifluoride and alkali-metal hydroborates is a convenient route to diborane, and has been fairly widely studied. The reaction with BF_3 etherate is quantitative[504]:

(1) $3NaBH_4 + 4BF_3.Et_2O \rightarrow 3NaBF_4 + 2B_2H_6 + 4Et_2O$

The reaction also occurs in diglyme and other glymes[67] (as a side reaction to the reaction of NaH and BF_3 to form $NaBH_4$) or in a low-temperature fused salt (i.e. < 250°C).[3] In these solvents, however, $NaBH_4$ may react with diborane to form the addition product NaB_2H_7.[67, 61] With excess $NaBH_4$, very little B_2H_6 evolves until the following reaction takes place[67]:

(2) $6NaBH_4.BH_3 + 8BF_3 \rightarrow 6NaBF_4 + 7B_2H_6$

BCl_3 can also be used, but in ethers it reacts with diborane to form chloroborane etherates.[67–8] Two reactions have been described[68]:

(3) $NaBH_4 + 3BCl_3 + 2R_2O \rightarrow 2H_2ClB.R_2O$

(4) $NaBH_4 + 3BCl_3 + 4R_2O \rightarrow 4HCl_2B.R_2O + NaCl$

Here, R = alkyl; BCl_3 is used in the stoichiometric amount of equation (2) to improve the yield.[67] The reaction can be hindered by a reaction between B_2H_6 and BCl_3 to form the same chloroborane etherates, but *only* in the presence of ethers (such as dimethyl and diethyl ether; diglyme; tetrahydrofuran; and tetrahydropyran).[68]

Patents have been issued for the general process using diglyme[259], tetraglyme[349], liquid ammonia[494], organic hydrocarbons with $AlCl_3$ catalyst[411], and with no solvent.[152]

Gaseous BF_3 will not react with $LiBH_4$, but the etherate reacts rapidly and quantitatively in the presence of excess etherate[504]:

(5a) $3LiBH_4 + 4BF_3.Et_2O \rightarrow 3LiBF_4 + 2B_2H_6 + 4Et_2O$

Competing reactions are[130]:

(5b) $3LiBH_4 + BF_3.Et_2O \rightarrow 2B_2H_6 + 3LiF + Et_2O$

(5c) $3LiBH_4 + LiBF_4 \rightarrow 2B_2H_6 + 4LiF$

(5d) $LiF + BF_3.Et_2O \rightarrow LiBF_4 + Et_2O$

At room temperature (5b) and (5c) proceed smoothly and rapidly. At 0°C, the rate of reaction (5b) is about one-quarter of that at room temperature, and (5c) is very slow.[138] At −30°C, other reactions are possible[423a]:

(5e) $2LiBH_4 + 2BF_3.Et_2O \rightarrow 2LiBHF_3 + B_2H_6 + 2Et_2O$

(5f) $2LiBHF_3 + 4LiBH_4 \rightarrow 6LiF + 3B_2H_6$

The reaction between $LiBH_4$ and BF_3 occurs as a side reaction to the reactions $LiAlH + BF_3$[521] and $LiH + BF_3$,[138] both of which are used to prepare diborane. The reaction in diethyl ether is patented[267] as the second of two steps in the preparation of diborane:

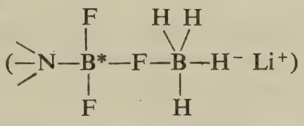
(6) $3LiBH_4 + BF_3 \rightarrow 2B_2H_6 + 3LiF$

Potassium hydroborate undergoes a reaction with BF_3 in diglyme to form diborane. The yield is 91%, even though the KBH_4 is less soluble than the Na salt. There is no $KBH_4.BH_3$ complex as in the Na case.[446] The reaction with KBH_4 has been patented.[534]

The reaction between lithium hydroborate and amino adducts of BF_3, namely $MeNH_2.BF_3$; $Me_2NH.BF_3$; and $Me_3N.BF_3$, has been studied. Only the last-named reacts[239]:

(7) $2(CH_3)_3N.BF_3 + 6LiBH_4 \rightarrow 2(CH_3)_3N.BH_3 + 3B_2H_6 + 6LiF$

An intermediate species



rearranges to form Me_3NBH_3 and LiB^*F_4, which reacts with $2LiBH_4$ to give $\frac{3}{2}B_2H_6 + 3LiF$.[542] A patent describes the reactions between sodium hydroborate, BF_3.THF, and the appropriate primary amine to give, after reflux in tetrahydrofuran, N:N′:N″-tripropylborazine, N:N′:N″-triphenylborazine and N:N′N″-tri-*tert*-butylborazine.[161]

Substituted boron halides react in the general way, and a series of such

$$(8)\quad 2R_2BX + 2MBH_4 \rightarrow 2R_2BH + 2MX + B_2H_6; \quad \begin{aligned} M &= \text{alkali metal} \\ R &= \text{alkyl or aryl} \\ X &= \text{halogen} \end{aligned}$$

reactions have been studied. Dichlorophenyl- and chlorodiphenyl-borane react in ether[423a, 593]:

(9) $2PhBCl_2 + 4LiBH_4 \rightarrow 2PhBH_2 + 4LiCl + 2B_2H_6$

B-trichloroborazines react to give borazines in 65% yield[486, 101]:

(10) $6LiBH_4 + 2B_3N_3H_3Cl_3 \rightarrow 2B_3N_3H_6 + 3B_2H_6 + 6LiCl$

The 1 : 3 adduct of borazine and HCl reacts with $NaBH_4$ in diglyme to give a hexahydroborazine[102]:

(11) $2B_3N_3H_6.3HCl + 6NaBH_4 \rightarrow 2B_3N_3H_{12} + 6NaCl + 3B_2H_6$

Dialkylchloroboranes (or mixtures of HCl and trialkylboranes, R_3B) react with lithium and $NaBH_4$:

(12) $2R_2BCl + 2NaBH_4 \rightarrow H_2B_2R_4 + 2NaCl + B_2H_6$

R is methyl, ethyl or *n*-propyl[334–6] (an analogous trialkylaluminium reaction is also reported).[333]

Lithium hydroborate reacts with B_2Cl_4 to give B_2H_6 and several higher boranes: B_4H_{10}, B_5H_{14} and $B_{10}H_{14}$ have been identified.[570] A patent[158] describes the reaction between esters of fluoboric acid, particularly F_2BOCH_3, and alkali-metal hydroborates to give diborane.

(c) *Boron–Oxygen Compounds*

The reaction of $NaBH_4$ with alcohols and acetic acid[56] or with trialkoxyboranes[345] gives the appropriate ester, which can be distilled. The overall reactions are (for primary and secondary alcohols):

(1) $3ROH + NaBH_4 + CH_3COOH \rightleftarrows (RO)_3B + CH_3COONa + 4H_2$
[R = CH_3, C_2H_5, *iso*-C_3H_7,[56, 345,] C_2H_3[56]]

for tertiary alcohols:

(2) $2ROH + NaBH_4 + CH_3COOH \rightleftarrows (RO)_2BH + CH_3COONa + 3H_2$

and, with prolonged reflux:

(3) $ROH + (RO)_2BH \rightleftarrows (RO)_3B + H_2$
[R = *tert*-C_4H_9, *tert*-C_5H_{11}[56]]

A reaction of $NaBH_4$ with trimethoxyborane or with tripenylborane will not proceed at 200°C in ether solvents.[14] In tertiary amines at elevated temperatures triphenylborane reacts; triethylamineborane and dimethylanilinoborane have been prepared.[14]

Patents[127] describe the reaction of $NaBH_4$ with trialkylborazines in monoglyme at 60–100°C (or without solvent at temperatures exceeding 100°C) to give B_2H_6 and various alkyldiboranes.

2. ALUMINIUM COMPOUNDS

The reaction of Na or Li hydroborate with $AlCl_3$, preferably in the absence of a solvent, proceeds at 100°C to form the volatile aluminium trihydroborate[507]:

(1) $AlCl_3 + 3MBH_4 \rightarrow Al(BH_4)_3 + 3MCl$

With excess aluminium chloride $ClAl(BH_4)_2$ and $Cl_2Al(BH_4)$ are formed.[21, 433] $NaBH_4$ in an ether solution of $AlCl_3$ most probably reacts to form a precipitate

(2) $3NaBH_4 + 4AlCl_3 \rightarrow 3NaCl + 4AlH_3 + 3BCl_3$

of aluminium hydride.[516] In diglyme at 25°C, at an Al : B mole ratio of 1 : 3, there is no precipitate and the mixture is used for hydroboration of olefins and reduction of organic molecules.[63–6] $LiBH_4$ reacts with aluminium chloride in ether at 25°C to form lithium aluminium tetrahydroborate[134]:

(3) $4LiBH_4 + AlCl_3 \rightarrow LiAl(BH_4)_4 + 3LiCl$

The compounds $H_{3-x}Al(BH_4)_x,NMe_3$ ($x = 1, 2, 3$) and $H_{2-x}Al(BH_4)_x,NMe_3$ ($x = 1, 2$) are prepared by the metathetical reaction of lithium hydroborate and the appropriate chloro derivative.[475–6]

In a mixture of diethylene glycol and dimethyl ether, or in tetrahydrofuran, sodium hydroborate reacts with aluminium chloro-*iso*-propylate $AlCl(CHMe_2)_2$ to form at 40–75°C a compound tentatively identified as di-*iso*-propoxyaluminium hydroborate[191], (*iso*-$C_3H_7O)_2AlBH_4$.

3. GALLIUM, INDIUM AND THALLIUM COMPOUNDS

Alkali-metal hydroborates react by metathesis with gallium, indium and thallium salts to form the corresponding hydroborates:

(1)[423a] $GaCl_3 + 3LiBH_4 \xrightarrow{15°C} Ga(BH_4)_3 + 3LiCl$

(2)[583] $Tl(NO_3)_3 + 3KBH_4 \xrightarrow{aqueous} Tl(BH_4)_3 + 3KNO_3$

(3)[592] $Tl,3(OEt) + 3LiBH_4 \xrightarrow[20°C]{Et_2O} \Gamma l(BH_4)_3 + 3LiOEt$

With excess lithium hydroborate, $TlCl_3$ reacts in Et_2O at 100°C to form the unstable compound $TlCl(BH_4)_2$.[608]

An impure indium hydroborate can be prepared at −25°C in Et_2O[607]

(4) $3LiBH_4 + InCl_3 \rightarrow In(BH_4)_3 + 3LiCl$

but the salt is best prepared in Et_2O–THF solvent from $InMe_3$ and B_2H_6 in 1 : 5 proportions. At −20°C, the reaction of lithium hydroborate with indium trichloride gives an unstable product which decomposes between −20 and −40°C to produce diborane[591]:

(5) $LiBH_4 + InCl_3 \rightarrow LiInCl_3.BH_4$

(6) $2LiInCl_3.BH_4 \rightarrow 2LiInCl_3H + B_2H_6$

Group IVB

1. CARBON COMPOUNDS

The reaction of sodium hydroborate and excess carbon dioxide in a sealed tube at 125°C[586–7] gives a product which may be: (i) $NaBO(OCH_3)(O_2CH)$; (ii) $NaB(OCH_3)_2(O_2CH)_2 + NaBO_2$; or (iii) $Na_3B_3O_3(OCH_3)_3(O_2CH)_3$. The absence of a non-reactive solvent makes unequivocal identification of these products difficult.[587]

At 125°C, there is no reaction between sodium hydroborate and CO, COS or CS_2, although the last of these reacts slowly in dimethylether.[587] Lithium hydroborate reacts slowly with carbon dioxide at 120°C to give $LiB(OCH_3)_3(O_2CH)$ and in dimethylether may react to give $LiBO(OCH_3)(O_2CH)$.[587] The reduction of CO_2 to HCOOH or to $LiB(OCH_3)_4$ by passing the gas over the lithium salt at 0°C has been reported.[79]

Treating lithium hydroborate with an ether solution of HCN gives $Li[B(CN)_4]$ and hydrogen. Heated to 100°C, this forms $Li(BH_3CN)$, which crystallizes from the ether solution.[615] The reaction with hydrazoic acid gives $LiB(N_3)_4$ and hydrogen.[597]

The reactions with the pseudohalogens, cyanogen, thiocyanogen and selenocyanogen have been studied[301–2] and the results are tabulated in Table VII.

Table VII.—Reactions of Pseudohalogens with Tetrahydroborates[302]

Metal hydroborate	Pseudohalogen	Solvent	Temperature (°C)	Products
$LiBH_4$	$(SCN)_2$	ether	−20 to +25	$LiB(NCS)_4 + H_2$
$NaBH_4$	$(SCN)_2$	ether	0 to +25	$NaBH_{4-n}(NCS)_n + H_2$
$LiBH_4$	$(SeCN)_2$	ether	−20 to +25	$LiBH_{4-n}(NCS)_n$, H_2, Se, HCN
$NaBH_4$	$(SeCN)_2$	ether	0 to +35	polymer of $(SeCN)_2$
$LiBH_4$	$(CN)_2$	ether	−20 to +25	brown solid
$NaBH_4$	$(CN)_2$	diglyme	0 to +35	brown solid
$NaBH_4$	$(CN)_2$	none	−23	slight reaction
$LiBH_4$	$(CN)_2$	none	−23	slight reaction

2. SILICON COMPOUNDS

Hydroborates react with silicon–chlorine compounds to form diborane and silane[595]:

(1) $SiCl_4 + 4LiBH_4 \xrightarrow[25°C]{Et_2O} SiH_4 + 2B_2H_6 + 4LiCl$

At low temperatures, −115°C, an intermediate $Li_2[Cl_4Si(BH_4)_2]$ has been proposed, decomposing at −60°C to $Li(Cl_3SiBH_4)$.[595] $LiBH_4$ reacts with hexachlorosiloxane at 0°C in ether to form silane and diborane; the Na salt will not react.[518] An acidic, aqueous hydroborate solution will not produce silanes, although analogous reactions will form AsH_3, SbH_3, GeH_4 and SnH_4.[280]

3. GERMANIUM COMPOUNDS

Germanium oxide in an acid solution will react with hydroborates to produce germanes.[541, 280, 452, 120] The most common, GeH_4, is obtained in 70% yield, with digermane, Ge_2H_6, also present.[452] Monodeuterogermane is prepared in 45% D_2O.[452] Similar yields of germane have been obtained by reacting $NaBH_4$ with tetrachlorogermane.[348, 118]

4. TIN COMPOUNDS

Stannous chloride[481] and stannous oxide[280] in acid solution, when reacted with $NaBH_4$, give stannane, SnH_4. A small amount of distannane, Sn_2H_6, is also produced.[481] A reaction, at 200°C without a solvent, between stannous chloride and Na or K hydroborate produces metallic tin and diborane.[273] The diborane yield, in vacuum, was 94% for $NaBH_4$ and 80% for the KBH_4. At atmospheric pressure under nitrogen, the product was a mixture of boron hydrides. The preparation of alkyl tin hydrides is effected by treating the appropriate alkyl tin chloride with sodium hydroborate in ether at −10°C. The mono-, di- and tributyl, as well as di- and trimethyl compounds have been made.[33]

5. LEAD COMPOUNDS

Sodium hydroborate reduces a $Pb(NO_3)_2$ solution to metallic lead at pH 5·6. This reaction affords analytical separation of lead from cadmium and barium.[485] Trialkylplumbanes have been prepared from the reaction of the chloro-derivative and $NaBH_4$ in liquid ammonia.[122–3] The product is obtained as an ammoniate (containing more than one ammonia addition molecule) and decomposes slowly at 0°C[123]:

$$(CH_3)_3PbCl + KBH_4 \rightarrow (CH_3)_3PbH + KCl$$

Group VB

1. NITROGEN COMPOUNDS

The stability of the hydroborates formed by the reaction of the hydroborate ion with ammonium and substituted ammonium compounds depends on the degree of substitution; only the quaternary ammonium hydroborates are stable at room temperature.

The reaction of lithium or, with more difficulty, sodium hydroborate in ether at 25°C produces monomeric ammonia–borane[524–5, 382]:

$$(1)\quad NH_4Cl + LiBH_4 \rightarrow H_3N.BH_3 + LiCl + H_2$$

At elevated temperatures (300°C) and in the absence of a solvent, the product is borazine[484]:

$$(2)\quad 3NH_4Cl + 3LiBH_4 \rightarrow B_3N_3H_6 + 3LiCl + 9H_2$$

The diammoniate of diborane, $B_2H_6.2NH_3$, has been detected in both the high- and room-temperature reactions.[484, 525] The reaction between $NaBH_4$ and NH_4HSO_4 produces no volatile boron nitrogen hydrides.[344] In liquid ammonia at −50°C, $NaBH_4$ reacts with ammonia salts[441, 492] to form the ammonium hydroborate which decomposes at −20°C:

$$(3)\quad NH_4X + NaBH_4 \rightarrow NH_4BH_4 + NaX\ (X = F \text{ or } \tfrac{1}{2}SO_4)$$

Lithium hydroborate reacts with mono-alkylammonium chlorides in ether to form trialkylborazines[344, 479, 257]:

$$(4)\quad 3RNH_3Cl + 3LiBH_4 \rightarrow R_3N_3B_3H_3 + 3LiCl + 9H_2 \quad (R = \text{alkyl})$$

The reaction must be heated, after solvent removal, to 250–290°C.[257] The low-temperature reaction in ether liberates only part of the total hydrogen and forms $H_2RN.BH_3$, which is then pyrolized to form borazine and hydrogen. The reaction prepares trimethyl[479], triethyl, tripropyl and tri-*iso*-propyl[257] borazine. At 85°C, sodium hydroborate and methylammonium chloride react to form 1 : 3 : 5-trimethyl*cyclo*borazine $[BH_2—NHCH_3]_3$[189]:

$$(5)\ 3(CH_3)H_3NCl+3NaBH_4 \rightarrow [BH_2—NHCH_3]_3+3NaCl+6H_2$$

The same product is obtained by the reaction between $NaBH_4$ and 1 : 3 : 5-trimethylborazine[189]:

$$(6)\ 2[BH—N(CH)]_3.HCl+6NaBH_4 \rightarrow 2[BH_2—NHCH_3]_3+6NaCl+3B_2H_6$$

In a similar manner, hexahydroborazine is prepared from borazine[102] in diglyme:

$$(7)\ 2B_3N_3H_6.3HCl+6NaBH_4 \rightarrow 2[BH_2—NH_2]_3+6NaCl+3B_2H_6$$

Prolonged refluxing in tetrahydrofuran causes $NaBH_4$ and $(H_2NCH_2)_2.HCl$ to form polymeric products of composition $(HNCH_2CH_2NB)_n$.[211] At −30°C in methylamine, sodium hydroborate and methylammonium chloride react to form methylammonium hydroborate:

$$(8)\ NaBH_4+CH_3NH_3Cl \rightarrow CH_3NH_3BH_4+NaCl$$

Decomposition of the product sets in at 0°C; at 25°C, its ammonia solution decomposes at a rate of about half that of the pure substance.[492]

Dimethylammonium chloride reacts with lithium hydroborate at 25°C in ether to form dimethylaminoborane[479]:

$$(9)\ (CH_3)_2NH_2Cl+LiBH_4 \rightarrow (CH_3)_2NBH_2+LiCl+2H_2$$

The reaction proceeds smoothly at 25°C in contrast to that of methylammonium chloride. A similar reaction with $(CH_2)_2NH_2.HSO_4$ has been reported.[344] A patent[491] covers the reaction of sodium hydroborate and dimethylammonium phosphate, in the absence of a solvent, to form dimethylaminoborane.

Trimethylammonium chloride reacts with $LiBH_4$ in ether at 25°C smoothly and directly to form trimethylamine borane[479]:

$$(10)\ (CH_3)_3NHCl+LiBH_4 \rightarrow (CH_3)_3N.BH_3+LiCl+H_2$$

A patent[243] describes a similar preparation from a boric or acetic acid solution of $NaBH_4$ and triethyl- or tributylamine. The reaction between $NaBH_4$, $B(OPh)_3$ and Et_3N at 200°C is reported to give Et_3NBH_3.[13]

The reactions between quaternary ammonium salts and hydroborates take place in water or dilute ethanol to produce quaternary ammonium hydroborates, stable to about 100°C.[23]

$$\begin{aligned}(11)\ & R_4NX+MBH_4 \rightarrow R_4NBH_4+MX; \quad R = CH_3,\ C_2H_5,\ PhCH_2;\\ & X = OH,\ \text{halogen},\ \tfrac{1}{3}PO_4,\ \ \tfrac{1}{2}CO_3,\ \tfrac{1}{2}C_2O_4; \quad M = Li,\ Na,\ \tfrac{1}{2}Ca\end{aligned}$$

A patent describes the reaction with tetraethylammonium chloride in tetrahydrofuran.[328] The reaction also takes place when the BH_4^- ion is held in a basic cation-exchange resin through which is passed the quaternary ammonium chloride.[264, 477]

Reactions between hydroborates and hydrazine derivatives produce hydrazine

$$(12)\ 2NaBH_4+(N_2H_5)_2SO_4 \xrightarrow[30-70°C]{\text{dioxane}} 2N_2H_4.BH_3+Na_2SO_4+2H_2$$

borane.[210] Patents describe the reaction with hydrazine hydrochloride in pyridine to produce, when the $NaBH_4$ is added to the hydrazine in 2:1 ratio, hydrazine diborane $BH_3.N_2H_4.BH_3$.[148, 70]

Substituted hydrazine hydrochlorides react in a manner similar to equation (12) to produce tetramethylhydrazine borane[422] and monophenylhydrazine borane.[148] If Na or Li hydroborate and dry hydrazine hydrochloride are heated to 180°C in the presence of a cobalt catalyst, borazine $(BH—NH)_3$ can be isolated.[141]

Hydrazinium magnesium hydrochloride reacts to form hydrazine borane[219]:

(13) $MgCl_2.4N_2H_4+2NaBH_4 \rightarrow 2N_2H_4.BH_3+2H_2+Mg(N_2H_3)_2+2NaCl$

Similarly[219],

(14) $2CH_3ONH_2.Cl+2NaBH_4 \rightarrow 2CH_3ONH_2.BH_3+2NaCl+H_2$

The product of this reaction is friction sensitive. A reaction with $(HONH_3)_2SO_4$ produces $(HONBH)_X$, which detonates at 100°C.[219]

A saturated solution of sodium hydroborate added to a cooled solution of hydrazinium hydrogen sulphate in hydrazine is reported[492], in unpublished work, to form the hydrazinium hydroborate; the reaction is exothermic

(15) $2NaBH_4+N_2H_4+N_2H_5.HSO_4 \xrightarrow{NH_3} 2N_2H_5BH_4+Na_2SO_4$

and the product could not be obtained free of hydrazine. Also prepared, in low purity, was the guanidinium hydroborate.[492] The reaction

(16) $NaBH_4+C(NH_2)_3Cl \rightarrow C(NH_2)_3BH_4+NaCl$

was run in *iso*-propylamine and the product obtained by vacuum distillation.

2. PHOSPHORUS COMPOUNDS

Lithium hydroborate and PCl_3 react in ether to form phosphine[423a]:

(1) $2PCl_3+6LiBH_4 \rightarrow 2PH_3+3B_2H_6+6LiCl$

An analogous attempt to form PH_5 from PCl_5 in ether at −80°C gave only equimolar amounts of phosphine and hydrogen.[598] Solutions of hydroborates added to an acid solution of phosphite and hypophosphite gave only traces of phosphine PH_3[280]; however, heating to combustion of a mixture of PO_4^{3-}, PO_3^{3-} and hypophosphite converted them to phosphide which, when dissolved in water, gave PH_3.[471, 470]

Alkyl and aryl chlorophosphines react in diglyme to give the corresponding phosphine borane.[76] The reaction proceeds in two steps, the first forming the phosphine, which reacts with the diborane in the second step:

(2) $2R_2PCl+2NaBH_4 \rightarrow 2R_2PH+B_2H_6+2NaCl$

(3) $6R_2PH+3B_2H_6 \rightarrow 2[R_2PBH_2]_3+6H_2$

The product from the ethyl reaction is a trimer, that from methyl is largely trimeric.[76]

Borane adducts are obtained from the reaction of lithium hydroborate and alkoxyphosphines (reactions 4, 5) or dialkylaminophosphines (reaction 6):

(4) $2(RO)PCl_2+4LiBH_4 \rightarrow 2(RO)PH_2.BH_3+B_2H_6+LiCl$

(5) $(RO)_2PCl+LiBH_4 \rightarrow (RO)_2PH.BH_3+LiCl$

(6) $(R_2N)_2PCl+LiBH_4 \rightarrow (R_2N)_2PH.BH_3+LiCl$

Relative stabilities[466, 423a, 605] are $(RO)_3P.BH_3>(RO)_2PH.BH_3>ROPH_2.BH_3$. Reacting a trialkoxy- or trialkylaminephosphine with $NaBH_4$ in a weak acid gives the corresponding borane adduct[466, 465], where R = alkyl and X = OR or NR_2:

(7) $2X_3P+2NaBH_4+2HOAc \rightarrow 2X_3P.BH_3+2NaOAc+H_2$

A reaction between alkylphosphinyl chlorides and $NaBH_4$ occurs in diglyme at 170°C, with $R=CH_3$ or C_2H_5, in ether, a reaction

(8) $6R_2POCl+9NaBH_4 \rightarrow 2(R_2PBH_2)_3+6NaCl+3NaBO_2+12H_2$

with phosphorus oxychloride, $POCl_3$, gives $H_3PO.BH_3$ at −115°C. This decomposes to a polymer $(H_2POBH_2)_n$ at −90°C; continued decomposition above −90°C gives a polymer with P : B : H = 1 : 1 : 2.[606] Benzenephosphonyl chloride reacts in ether to give the phosphine $(C_6H_5)PH_2$,[181] which decomposes at room temperature to $(C_6H_5)P(OH)_2$.

The reaction between $LiBH_4$ and tetra-alkyldiphosphine disulphide is reported[454, 84] as a method for preparing trimeric alkyl compounds. $NaBH_4$ and phosphonium iodate react at −78°C in monoglyme to give[241] $Na^+(BH_3PH_2BH_3)^-$.

Phosphonium hydroborates are prepared by metathetic reactions. Reported are: $(C_6H_5P.CH.PC_6H_5)BH_4$ (from the bromide with $NaBH_4$ in methanol)[121]; $C_6H_5PBH_4$ and $(C_6H_5CH_2)CH_3PBH_4$ (from the bromides with $NaBH_4$ in diglyme + chloroform, and diglyme, respectively)[88]; and $(C_6H_5)_4PBH_4$ (from the fluoride with KBH_4 in water).[237]

3. ARSENIC, ANTIMONY AND BISMUTH COMPOUNDS

Stibine and arsine can be prepared by the action of hydroborate on an acid solution of the arsenite or antimonite[280] or from $LiBH_4$ with the trichlorides in ether at $-80°C$[599]:

(1) $2MCl_3 + 6LiBH_4 \rightarrow 2MH_3 + 3B_2H_6 + 6LiCl$

With bismuth trichloride, only the decomposition products of BiH_3 and $Bi + H_2$ are observed.[599] In the aqueous-phase preparation using antimony trichloride, sufficient acid to prevent the precipitation of basic antimony chlorides improves the yield.[251] Stibine is prepared from a solution of potassium antimony tartrate $KSbO(C_4H_4O_6)$.[222] In tracer studies, stibine was prepared from potassium antimony tartrate and potassium hydroborate in heavy water and NaOD, slowly dropped into heavy water and D_2SO_4. Although the exchangeable H was 97%D, the SbH_3:SbD_3 product ratio was 15:1. Two reaction paths are proposed[402], the major involving only BH_4^- to form SbH_3, the minor involving B_2D (from D_2SO_4 and KBH_4) and Sb^{3+}. Reactions of the

(2) $(C_6H_5)_nMX_{3-n}(3-n)(LiBH_4) \rightarrow (C_6H_5)_nMH_{3-n} + (3-n)(LiX)$

kind have been run in ether at about $-50°C$. Reactions noted are (i) $n = 1, 2$; M = As, X = Cl[600]; (ii) $n = 1$, M = Sb, X = I[601]; (iii) $n = 2$, M = Sb, X = Cl.[602] When M = Bi; $n = 1, 2$; X = Br, Cl, there is no corresponding bismuth product, only its decomposition products, $(C_6H_5)Bi + H_2$ and $(C_6H_5)_2Bi + H_2$; the last disproportionates to give $(C_6H_5)_3Bi$ and $[(C_6H_5)Bi]_n$. The latter is a black, high-molecular-weight, ether-insoluble material.[603] Reactions similar to reaction (2) produce the appropriate alkylarsines from $\underbrace{CH_2(CH_2)_4As}Cl$ and $\underbrace{CH_2(CH_2)_3As}Cl$ in ether at -50 and $-60°C$.[604] In these compounds the metal–hydrogen bond is rather unstable, and even at low temperatures of preparation the compounds are often co-ordinated with borane fragments.

Group VIB

1. OXYGEN (ELEMENTAL)

Heating sodium and potassium hydroborates to 294 and 356°C initiates oxidation, and completion is attained at 420 and 480°C, MBO_2 being the final product.[437]

2. WATER

As explained in a previous section (General Properties, p. 355), the BH_4^- ion is stable in water at pH greater than 12·5. At lower pH, hydrolysis, accompanied by hydrogen evolution, takes place accordingly to the overall reaction:

(1) $BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 4H_2\uparrow$

This is the most intensively studied of the hydroborate reactions, and its mechanism is not yet fully known, several techniques of investigation suggesting different courses. The earliest observation was that the rate of reaction increases as the hydrogen ion concentration increases.[72, 71, 183, 298, 409, 410, 447, 503, 375] The reaction is not, however, a specific hydrogen-ion reaction, as the hydroborate ion has been shown to undergo general acid catalysis.[283, 194, 104, 109, 553] The reaction has been described, kinetically, as first-order in both BH_4^- and H^+ concentrations.[298, 409, 71–2, 410, 357] A more complete description of the rate includes both acid-dependent and acid-independent terms, each first-order in BH_4^-.[357–8]

$$\frac{-d(BH_4^-)}{dt} = k_1[H^+][BH_4^-] + k_2[BH_4^-]$$

$k_1 = 2{\cdot}19 \times 10^{11}$ exp $\{-4{,}000/T\}$ mol^{-1} min^{-1}; $k_2 = 1{\cdot}72 \times 10^7 T$ exp $\{-10{,}380/T\}$ min^{-1}. For the active intermediates in each reaction:

	Reaction 1	*Reaction 2*
$\Delta H^{\#}$	$7{\cdot}9 \pm 1$ kcal mol^{-1}	$22{\cdot}1 \pm$ kcal mol^{-1}
$\Delta S^{\#}$	$-4{\cdot}0 \pm 3$ cal mol^{-1} deg^{-1}	$-18{\cdot}4 \pm$ cal mol^{-1} deg^{-1}

The above data were calculated from rate data over pH range 3·8 to 14 and at temperatures 10·5, 25·0, 37·9 and 49·7°C.[358] Although there was no evidence of a stepwise reduction of BH_4^-, the rate-controlling reaction of the acid-catalyzed hydrolysis was postulated to involve the short-lived intermediate BH_5[358, 357]:

$$(2)\ BH_4^- + H^+ \overset{\text{slow}}{\rightleftarrows} BH_5{\cdot} \xrightarrow{\text{fast}} BH_3 + H_2$$

This intermediate is also postulated in other works.[410, 404, 135] Proton exchange between BH_4^- and H_2O also proceeds by two paths, one acid catalyzed and the other pH independent. The rate of exchange may be expressed by an equation similar to that for hydrolysis, but at room temperature the overall rate is about 6% of that for hydrolysis[281], and the activation energy is less than that for hydrolysis.[281]

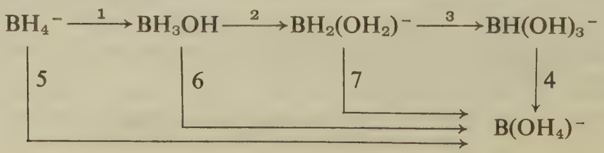
Isotope studies show that in water BD_4^- hydrolyzes at a rate greater than BH_4^- [104, 358, 107] and BH_4^- hydrolysis is faster in H_2O than in D_2O[358, 107, 103a] although with some disparity in the reported rate ratios. Since the reaction is catalyzed by metal ions, care must be exercised in determining isotope rate effects.[103a] BH_4^- hydrolysis in D_2O gives 96% D_2[358] (92% with Pt catalyst)[323], while BD_4^- in H_2O gives 92% H_2.[358] A monohydrated species similar to that of equation (2) is also postulated[104, 103] and is suggested by trapping, in trimethylamine, a species BH_3—H_2—Me_3N.[103] The inverse isotopic effect for the hydrolysis of KBH_4 and KBD_4, $KBH_4/KBD_4 \simeq 0{\cdot}7$, is attributed to two separate actions. The primary, normal action affects the primary B—H bond breaking (in the rate-determining step). The secondary affects the other B—H bonds, which are not breaking in the rate-determining step. In the postulated aquated borane H—B$^-$ bonds change to H—B with more difficulty than the corresponding change of D—B$^-$ bonds to D—B.[106–7]

In 8 M HCl, KBH_4 hydrolyzes at −70°C to give only two moles of hydrogen, the remaining two being released upon heating to 20°C. These studies are interpreted to show the presence of BH_2^+ ions at low temperatures or, more generally, $Base_2.BH_2^+$ or $(H_2O)_2.BH_2^+$.[282–3]

A successive stepwise reaction is used by many workers to explain intermediates postulated from polarographic and other measurements. In the hydrolysis of $NaBH_4$, the first $\frac{1}{2}H_2$ is liberated more easily, giving a residue postulated as NaH_3BOH following infra-red analysis. Upon heating above 170°C, H_2O is lost, leaving a residue of $NaBO_2$ and $NaBH_4$.[209] Paper chromatography was used[400] to study the products of $NaBH_4$ hydrolysis; $NaBH(OH)_3$ was isolated. $LiBH_4$ in pure water at 0°C is stable, but at 20°C one-quarter of the total hydrogen is driven off, leaving $LiBH_3OH$; at 100°C one-half of the hydrogen is lost, leaving $LiBH_2(OH)_2$.[375] Acidified catalysts, Ni, Co, Cu, Ag, cause loss of all hydrogen.[375]

Polarographic studies have been used to identify intermediates.[398, 194, 404, 386, 193, 195, 396, 447] A wave at 0·65 V (versus standard calomel electrode) exists only below pH 12·5, above which BH_4^- is stable. The wave has been variously interpreted, and involves a BH_3-containing species, $BH(OH)_3^-$.[193, 195, 396, 398, 386, 194, 387]

A postulated stepwise reaction for alkaline hydrolysis is described, with a rate-controlling step $BH_4^- \rightarrow BH_3OH^-$.[404, 399] This reaction has two steps, one of which is $BH_4^- + H^+ \rightarrow H^+{\cdot}BH_4^-{\cdot}$; stabilities of intermediates are discussed.[404] The postulated reaction scheme with individual and overall rate constants determined at 15°C is:



The reactions are first-order in H^+ and the various B species; reactions were measured at 15, 25 and 35°C. At 15°C the overall and stepwise rate constants are[406, 405]:

k_1	$5{\cdot}31 \times 10^7$ mol^{-1} min^{-1}
k_2	$3{\cdot}57 \times 10^{11}$ mol^{-1} min^{-1}
k_3	$10{\cdot}06 \times 10^7$ mol^{-1} min^{-1}
k_4	$5{\cdot}69 \times 10^{10}$ mol^{-1} min^{-1}
k_5	$5{\cdot}15 \times 10^7$ mol^{-1} min^{-1}
k_6	$9{\cdot}44 \times 10^7$ mol^{-1} min^{-1}
k_7	$10{\cdot}06 \times 10^7$ mol^{-1} min^{-1}

The anodic behaviour of hydroborate ion was stable to measurement only at a Pt electrode. The potential, which is not a function of concentration or pH, BH_4^- and borate concentrations, is interpreted as a 2-electron process in which BH_3 is formed on the electrodes and then hydrolyzed to the H_3BOH^- ion and H^+.[135, 136]

$$BH_4^- + Pt \rightarrow Pt \cdots BH_3 + 2e + H^+$$

3. SULPHUR (ELEMENTAL)

In the absence of a solvent, $LiBH_4$ and sulphur react exothermically at 200°C, depending upon the stoichiometry[425]:

(1) $LiBH_4 + 4S \rightarrow LiBS_2 + 2H_2S$

(2) $LiBH_4 + 2S \rightarrow LiBS_2 + 2H_2$

In diethyl ether at room temperature the reaction is:

(3) $3LiBH_4 + 3S \rightarrow LiB_3S_2H_6 + Li_2S + 3H_2$

and at −50°C, in diethyl ether:

(4) $LiBH_4 + S \rightarrow LiH_3.BSH$

The last compound is unstable at room temperature and decomposes to form the products of reaction (3).[425]

Sodium, potassium and lithium hydroborates react exothermically at 250°C to form MBS_2, in a reaction analogous to reaction (1)[545, 425, 546]:

(5) $MBH_4 + 4S \rightarrow MBS_2 + 2H_2S$; M = Na, K, Li

4. SULPHUR COMPOUNDS

Hydrogen sulphide bubbled through a solution of lithium hydroborate in tetrahydrofuran at −22°C reacts in a manner similar to water and forms the thioborane $LiHSBH_3$.[542] One mole of hydrogen gas per mole hydroborate is immediately released, and above 0°C further hydrogen is released. Thioborane is more stable than its oxygen analogue. The isolated product is possibly contaminated with $Li(HS)_2BH_2$.[542]

Hydroborates reduce S—O species, commonly to S^{2-}. Heating a mixture of either SO_4^{2-}, SO_3^{2-} or $S_2O_3^{2-}$ and KBH_4 to spontaneous combustion reduces the sulphur species to S^{2-}.[471] Thiosulphate, trithionate (only with $SnCl_2$) and tetrathionate (only with dichromate) are reduced to S^{2-}, and the reductions form the basis of a chemical analysis of 3-component mixtures.[585] In a highly alkaline solution, HSO_4^- is reduced to S^{2-} by $NaBH_4$. In a 0·2 M NaOH aqueous solution, the bisulphate is reduced to dithionite $S_2O_4^{2-}$.[438] A patented process produces sodium dithionite from SO_2 and $NaBH_4$ under water- and oxygen-free conditions. In an example, the gas is passed over the solid.[224]

Metathetic reactions occur with sulphonium compounds. Trimethylsulphonium fluoride and $NaBH_4$ produce the sulphonium hydroborate[236]:

(1) $(CH_3)_3S.F + NaBH_4 \rightarrow (CH_3)_3S.BH_4 + NaF$

which decomposes above 90°C to methane and dimethyl sulphide borane. Triphenyl sulphonium fluoride reacts to form triphenylsulphonium hydroborate.[237]

In a vacuum, $NaBH_4$ added to H_2SO_4 gives B_2H_6 contaminated with SO_2. Decreasing the acid concentration decreases the yield and SO_2 impurity, and increases hydrolysis of the hydroborate. SO_2-free diborane can be prepared in reduced yield if $MeSO_3H$ is substituted for H_2SO_4.[588] A similar reaction is patented[517], and mentions substitution of $ClSO_3H$ for the sulphuric acid; aliphatic acids, esters and salts are reaction moderators.

5. SELENIUM COMPOUNDS

Selenium oxide is reduced by sodium hydroborate in a dry chamber under N_2 to give the metal[407]:

(1) $SeO_3 + NaBH_4 \rightarrow Se + NaBO_2 + H_2O + H_2$

Group VIIB

1. ELEMENTAL HALOGENS

Sodium and lithium hydroborates react with iodine in hexane[303], and,

(1) $3MBH_4 + 8I_2 \rightarrow 3BI_3 + 4HI + 3MI + 4H_2$; M = Li, Na

in the absence of solvent, Na and Li hydroborates react similarly at 200 and 120°C[192], respectively. The reaction between $LiBH_4$ and iodine in *n*-hexane at room temperature is reported to give no hydrogen and some diborane.[467] The reaction may be conducted more rapidly under reflex, but with reduced yield.[467] In di- or triglyme at room temperature, and at near vacuum, the reaction produces diborane and hydrogen[182]:

(2) $2NaBH_4 + I_2 \rightarrow 2NaI + B_2H_6 + H_2$

Bromine may also be used. Sodium hydroborate will not react with bromine at temperatures up to 80°C.[303]

In ether at $-60°C$, $LiBH_4$ reacts with chlorine to give diborane[423a]:

(3) $2LiBH_4 + Cl_2 \rightarrow B_2H_6 + 2LiCl + H_2$

Two consecutive side reactions occur[423a]:

(4) $5Cl_2 + B_2H_6 + 2R_2O \rightarrow 2R_2O.BCl_3 + H_2 + 4HCl$

(5) $2HCl + B_2H_6 + 2R_2O \rightarrow 2R_2O.BH_2Cl + 2H_2$; R = alkyl

$NaBH_4$ reacts with halogens (Cl, Br or I) and ethers or alcohols to form alkyl halides[332] (R′ = alkyl, aryl, H).

(6) $3ROR' + 2X_2 + NaBH_4 \rightarrow 3RX + B(OR')_3 + NaX + 2H_2O$
(R = alkyl; R′ = alkyl, aryl, H)

A similar reaction occurs when ICl is used; and if there are more than two carbon atoms in the organic group, isomerization occurs[332], for example, $(n\text{-}C_4H_9)_2O$ is converted to *sec*-C_4H_9I.

2. HALOGEN COMPOUNDS

The reaction of hydroborates with aqueous acid solutions has received attention in the section on hydrolysis (p. 381). Both Na and Li hydroborate react in non-aqueous media and at low temperatures, i.e. -40 to $-80°C$, with hydrogen chloride, bromide, or iodide to form B_2H_6.[69, 303, 423a] The non-aqueous reaction is run in ethers[303, 423a], amines[423a] or alkanes[303]:

(1) $2MBH_4 + 2HX \rightarrow B_2H_6 + 2MX + 2H_2$
[M = Li, Na]

Diborane is also a product of the reaction between Na or $LiBH_4$ and metal halides, where the metal is preferably one lacking a stable hydride.[182]

In aqueous solution, hydroborates reduce OCl^- and OBr^- to Cl^- [86] and Br^- [423a]:

(2) $BH_4^- + 4OCl^- \rightarrow BO_2^- + 4Cl^- + 2H_2O$

The reaction may be applied directly as an analytical method with Bordeaux-red as indicator.[86] $NaClO_2$ and ClO_2^- are reduced by KBH_4 to NaCl or HCl.[85] Since chlorates are not affected, the two previously mentioned reactions can be used in analysis in the presence of chlorates.[85–6] The iodate ion is reduced by Li, Na or K hydroborates in aqueous solution accordingly to the equation[343, 379]:

$$(3)\ 3BH_4^- + 4IO_3^- \rightarrow 4I^- + 3H_2BO_3 + 3H_2O$$

For the analysis of iodate, the iodine formed in this reaction is heated with KIO_3, and the I_2 formed is titrated with $Na_2S_2O_3$ to a starch end-point.[343] The kinetics of the reaction are first-order in IO_3^-, BH_4^- and H^+, and are independent of the I^- ion concentration. Hydrolysis to the borate occurs simultaneously.[185]

Diphenyliodinium hydroborate has been prepared at 0°C from the fluorides and KBH_4.[237]

REACTIONS WITH TRANSITION METAL COMPOUNDS

Reactions between hydroborates and transition metals usually result either in reduction of the metal or formation of a hydride (or borohydride) or both. Two reviews cover the hydride complexes of transition metals.[199, 215] The reduction of transition metals by the hydroborate ion is summarized in Table VIII.

Table VIII.—Reduction of Transition Metals by Tetrahydroborate Ion

Metal	Reduction	Conditions	References
Ti	IV → III	Ether, $Ti(BH_4)_3$	244
V	V → IV	Aqueous soln	587
Cr	VI → III	Non-alkaline aqueous soln	477a
Mn	VII → IV	Basic aqueous solns	594
	VII → VI		547
	VII → II		
Fe	III → II	Aqueous soln weakly acid	395
	III → II	Ether, −40°C; $Fe(BH_4)_2 + B_2H_6$	483
	$Fe(CN)_6^{3-} \rightarrow Fe(CN)_6^{2-}$	Aqueous solns	405, 183, 401, 403, 258
Co	II → O	Ether, Co_2B; aq. CoB_2 compd	503, 548, 549
Ni	II → Ni_2B	Aqueous soln	442, 548, 350, 245,(a) 381, 55
	II → $Ni(BH_4)_2$ → Ni_2B;	dry heat 320–470°C	547
Mo	VI → III		
	VI → V	Non-alkaline aqueous solns	477a
Pd	II → O		54, 53
W	VI → W blue (VI+V states)		477a
Pt	II → O	Aqueous solns	54, 53

(a) Analysis shows Ni metal present as catalytic residue, probably Ni_3B.

Many of the products in Table VIII are catalysts for reactions such as hydrogenation[53] and the hydrolysis of hydroborate.[53, 249] The relative rates of hydrolysis, as expressed by the half-life of the hydroborate ion, are given in Table IX.

The isotope ratio of the gas evolved during hydrolysis in D_2O varied as the catalyst, Co^{++}, Pt on carbon or Pd on carbon.[323] Cu^{++} and Ag^+ also catalyze hydrolysis, both to a lesser extent than Co^{++}.[375]

A patented preparation of diborane involves the halide of a reducible metal, such

Table IX.—Half-Life of Hydroborate Ion During Hydrolysis in Presence of Metal Ions

Metal ion	Half-life (min)
Fe(II)	38
Co(II)	9
Ni(II)	18
Ru(III)	0·3
Rh(III)	0·3
Pd(II)	180
Os(VIII)	18·5
Ir(IV)	28
Pt(IV)	1

as $FeCl_3$. The reaction with a hydroborate run in ether at -5°C or with no solvent at 220–320°C, gives B_2H_6, NaCl and $FeCl_2$.[3]

REACTIONS WITH RARE-EARTH COMPOUNDS

Rare-earth chlorides react by metathesis with $LiBH_4$ according to the equation[74, 474]:

(1) $MCl_3 + 2LiBH_4 \rightarrow MCl(BH_4)_2 + 2LiCl$

where M = Sm, Gd, Tb, Dy, Er.

USES OF TETRAHYDROBORATES

The commercial uses of alkali-metal hydroborates are mostly potential, the transformation to actuality awaiting either a massive reduction in price, or confidence of the same by potential users.[566] The literature, particularly the patent literature, describes many ways in which the compounds can be employed in industrial schemes. The reducing properties of the hydroborates are useful for natural products as well as organic and inorganic compounds. The hydrogen-generating ability of hydroborates treated with acid is also potentially useful.

A class of reactions of industrial importance, reduction of organic molecules, is treated widely in the literature. The hydroborates are also involved in numerous potential schemes to provide, by reduction of metals, active catalysts for the specific reduction of organic molecules. Both classes of reactions are rather arbitrarily omitted from this review as being quite solidly in the realm of organic chemistry.

The uses of hydroborates, particularly that of Na, in the paper industry are based upon the ability to reduce cellulose oxidation products, aldehydes and ketones, produced in pulp-cooking and bleaching processes. Specifically, $NaBH_4$ has improved and stabilized pulp brightness, increased pulp yield and rate of delignification in the Kraft process, and reduced cellulose degradation in the alkaline refining of acid prehydrolyzed pulps.[428, 230, 232] There appears to be a limit to its effectiveness in treating pulps following oxygen bleaching.[469] Papers describing the action of hydroborates in paper pulping are to be found in Refs. 198, 284, 230, 231, 562, 356, 347, 216–17, 233, 618, 234, 355.

A body of literature exists describing the use of hydroborates to bleach and stabilize paper pulps: 351, 338, 137, 463, 341, 354, 339, 11, 340, 91, 286, 178, 367, 176, 114, 528.

The bleaching properties of hydroborates have been patented for use on clays[177, 175] and described[352, 589] and patented[368, 285] for cotton. Possible uses in the manufacture of textile cotton are reductive bleaching, improving fibres damaged by excessive oxidative bleaching and in dyeing.[575]

Miscellaneous bleach and colour-stabilizing uses mentioned are for fibres of copolymers of polyvinyl alcohol[523, 324], for phenol[431] and ethanolamines.[413] The chemical stabilization[279, 511] of water-soluble cellulose ethers, alkali cellulose[393] and cellulose sheets[472–3] (by deposition of Ag, Au or Cu metals in cellulose membranes to be used in electrolytic storage batteries and fuel cells) has been patented.

In vat dyeing, $NaBH_4$ as a reducing agent makes use of the relatively greater stability of the hydroborate towards air and water, easing the need for large excesses of hydrosulphite and caustic soda, thus allowing higher temperatures.[229] In one study, however, with indanthrene dyes used at 24–95°C, pH 11–13, the increased stabilization achieved by hydroborate was not conclusively shown.[28] Patents covering the vat dyeing process have been issued, see Refs. 204, 146, 539, 203, 420, 540, 117.

Hydroborates are patented ingredients in cosmetic hair setting preparations.[530, 536]

Sodium hydroborate has been studied for use in fuel cells, both for generation of H_2 in a cation-exchange membrane cell[436] and for discharge at a Ni electrode.[265] Patents cover the fuel-cell oxidation of K and Na hydroborates[271–2], and hydrogen generation from them.[571] Power from the chemical combustion of liberated hydrogen is patented, using oxygen[567], HNO_3, liquid O_2, H_2O_2[12] and O_2 plus hydrazine.[309] Slurries of hydroborates in hydrocarbons are burned in oxygen[414] and ignition systems with a variety of oxidizers: HNO_3, H_2O_2, N_2O_5, etc.,[201] are patented. Sodium hydroborate is also patented as a burning-rate catalyst in ammonium nitrate propellants.[223]

$NaBH_4$ has patented photographic uses, to reduce silver halide emulsions[187, 306, 240], and in a photographic reversal process.[305]

The hydrogen released from hydroborates upon acidification has received attention in a number of applications. The process is patented[2], one variation using a catalyst-coated rod immersed to a depth which gives the desired hydrogen production rate.[329] The force of the gas generated is studied as a possible attitude control system for spacecraft[417], and a field generator of hydrogen gas is patented.[160] Hydrogen gas generated in a capped oil well is said to improve recovery by loosening closed pores and removing obstacles to oil flow.[576] The generation of H_2 within a variety of rubber or resin matrices provides a means for production of cellular materials.[263, 580, 577–9, 165, 419]

The hydroborates have been patented as metal-surface cleaning and descaling agents[151, 261] and as corrosion inhibitors in systems containing non-demineralized water.[35]

A promising use is in the electro-less plating of Ni (and Co) on to irregularly shaped or non-conducting surfaces. Nickel salts are reduced in aqueous solution by hydroborate or amino-boranes. The deposits, Ni–B alloys, are non-porous, hard, and of even thickness.[326–7] Patents have been issued[164, 560, 125, 154–5, 248, 564], for coating chiefly Ni and Co, and also Fe.[248]

QUANTITATIVE ANALYSIS FOR HYDROBORATE ION

Two common analytical techniques are gasometric and volumetric using potassium iodate.[368c] In the former, a basic aqueous solution of hydroborate is slowly made acid, and the volume of evolved hydrogen measured.[108] The volumetric method[368c] involves adding potassium iodate in excess. The liberated iodine is titrated with sodium thiosulphate to a starch (amylose) end-point.[86, 343] A similar technique calls for addition of basic OCl^- to excess. The excess is determined by iodimetric measurement, I_2, IO_3^-, ClO_2^-, ClO_3^-, BrO_3^-, CrO_4^{2-}, MnO_4^- and $S_2O_8^{2-}$ interfere.[235] Adding Ag^+ to excess in the presence of ethylenediamine, filtering the silver precipitate, and determining the excess Ag^+ by the Volhard method provides an analysis in the presence of IO_3^- [52]: the success of the technique illustrates the slowness of the BH_4^-–IO_3^- reaction.[52] Metal hydroborates or boron halides generate an e.m.f. at a silver or antimony electrode which, by calibration, can be related to the concentration.[30] The reaction of BH_4^- with acetone provides the basis of a spectrophotometric analysis: the amount of acetone consumed is determined at 265 nm.[330]

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SECTION B7

DERIVATIVES OF BORANE(3) CONTAINING GROUP-IV AND GROUP-V SUBSTITUENTS

BY L. H. LONG

INTRODUCTION

With the exception of diboron compounds (borylboranes) (cf. p. 56), no substituted derivatives of borane(3) containing covalently bound substituents with elements from Groups I–III inclusive linked directly to the boron are known. However, the number of characterized derivatives in which an element from Group IV, V, VI or VII is so linked is exceedingly large. Examples with substituents from Groups IV and V are considered in the present section, while those with substituents from Groups VI and VII are treated in other relevant sections of this work (Sections A17, B10, B11, B13, B15).

No case of direct substitution of free BH_3 has been definitely observed so far. This must be attributed to experimental difficulties in working with such a transient and highly reactive species, rather than to any inherent inability of BH_3 to participate in substitution reactions, since many of the substituted derivatives are isolable compounds of much greater stability. Substitution of borane(3) adducts is sometimes feasible, but this normally produces an adduct of the substituted derivative. A rare case in which the free derivative is produced directly from a BH_3 adduct, is the formation of BMe_3 from $H_3B.NMe_3$ by a CH_2-insertion reaction involving the Simmons-Smith reagent (CH_2ZnI_2).[1] In general, however, substituted boranes are not prepared from borane adducts, but from other starting materials.

Since the total number of known derivatives of borane(3) is far too great for comprehensive treatment here, the present account is confined mainly to the simpler members of this class of compounds.

Full substitution of BH_3 leads to the trisubstituted derivatives of type BR_3, which are in general monomeric compounds and often relatively stable. Partial substitution gives rise to the rather less stable mono- and disubstituted derivatives of type BH_2R and BHR_2 respectively. Whether such compounds are monomers depends to a large extent on the nature of the substituent R. If they are dimers containing 3-centre bonds, then, strictly speaking, they are derivatives of B_2H_6. When the element attached to the boron cannot form more than a single σ bond with it, as when the element is carbon, then it is normal for the partially substituted borane(3), whether of type BH_2R or BHR_2, to be dimeric through hydrogen-bridge bonding, so giving rise to a terminally substituted diborane(6).

When, however, the attached element has one or more lone pairs of electrons, so that a measure of π bonding with the boron atom becomes at least feasible on account of the vacant orbital on the latter, the tendency for dimerization or oligomerization through the formation of 3-centre bonds is so far reduced that the disubstituted derivatives are normally monomeric. On the rather rare occasions when dimerization of such disubstituted boranes occurs, this arises by some other means, e.g. by coordination (p. 98), and for structural reasons the resulting dimers are not strict derivatives of B_2H_6. B_2H_6.

With the monosubstituted derivatives the position is more complex. If the substituent is attached by a Group-V atom, for example, nitrogen, the monosubstituted derivative may be a monomer or alternatively (with nitrogen) a weakly associated dimer through nitrogen-bridge bonding, resulting in a $\mu\mu$-disubstituted diborane (p. 93); or sometimes with nitrogen and commonly with phosphorus and arsenic it may be a trimer or tetramer, or a higher polymer—or a mixture of the same—through bridge bonding involving the Group-V atom. Genetically, the trimers and tetramers are fully bridge substituted derivatives of B_3H_9 (p. 180) and of a hypothetical B_4H_{12} (p. 228) respectively. With Group-V substitution, therefore, the situation differs according to the vertical position of the element within the Group. However, there is also a horizontal difference with respect to Group-VI and Group-VII substitution. Thus, monosubstituted derivatives with sulphur substituents are normally dimeric. With the most electronegative substituents such as —OMe and —F, dimerization does not occur, and—unless immediate stabilization is effected by coordination with a Lewis base—the monosubstituted derivatives are so unstable as to be non-isolable on account of immediate disproportionation to the disubstituted derivatives and B_2H_6. Alternatively, if the disubstituted derivative is also too unstable to be isolated (as when the substituent is iodine) the disproportionation proceeds immediately to the trisubstituted derivative.

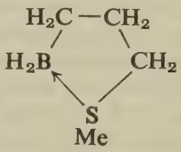
DERIVATIVES WITH CARBON SUBSTITUENTS: ORGANOBORANES

General

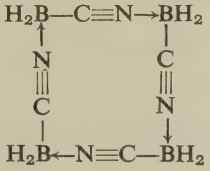
Substituted derivatives of borane(3) that contain organic substituents constitute a vast class of compounds known as organoboranes, which in turn are part of a still larger group usually termed organoboron compounds. To deal even with the organoboranes and their very extensive and varied chemistry adequately would require a separate volume, which, since much of the chemistry is essentially organic in nature, would be hardly justified in this inorganic treatise. Some brief mention of organoboranes must however be made, and the account which follows should be regarded as, at most, indicative.

Organoboranes are in general highly oxygen-sensitive, and the more volatile members of this class are spontaneously inflammable.

Because the monosubstituted derivatives BH_2R [R = organic radical] are almost invariably dimers $B_2H_4R_2$, these are included as derivatives of B_2H_6 (p. 88 ff). Rare exceptions are however known. Thus, possibly for steric reasons, the compound $H_2BCH(CMe_3)CH_2CMe_3$ is monomeric;[2] in other cases chelation may prevent dimerization when the substituent R contains a donor atom some distance from the boron atom, as in 3-(methylthio)propylborane(3) $MeS(CH_2)_3BH_2$, which is preponderantly of structure



and is distillable.[3] Some other monomeric species may have a transitory existence only, such as methylborane(3) BH_2Me in its formation from boron carbide and hydrogen at high temperatures and low pressures.[4] But even where the monomer is completely unknown, this has not prevented calculations of a theoretical nature from being made on occasion, as with BH_2Me[5, 6] and a hypothetical vinylborane(3) $H_2BCH{=}CH_2$,[7, 8] for which the barrier to internal rotation has been calculated to be 7·6 kcal mol^{-1}. Dimerization of the monosubstituted derivatives can generally be prevented by coordination, which may also prevent disproportionation. Amines are effective. Thus phenylborane(3) can be isolated as its pyridine adduct $C_5H_5N.BH_2Ph$, m.p. 80–83°C.[9] Adducts with amines are monomeric and hydrolyze at a measurable rate, enabling the mechanism to be studied.[10] Ethers such as tetrahydrofuran also stabilize partially substituted boranes to some extent, but on account of their weaker bonding powers with boranes are less effective at hindering disproportionation, and merely slow it up.[11] The compound cyanoborane, prepared from the reaction of $Na[H_3BCN]$ with HCl, is exceptional in being a mixture of cyclic oligomers $(H_2BCN)_n$ [$n=4$–9],[12] the simplest having the structure



The crystal structure of the hexamer $(H_2BCN)_6$ has been determined.[13]

The simplest compound containing more than one —BH_2 group attached to the same carbon atom, diborylmethane $CH_2(BH_2)_2$, has not been prepared, but has been given an *ab initio* MO treatment.[14] Other diborylalkanes $RCH(BH_2)_2$ have been made by the hydroboration of terminal alkynes (p. 104), and are useful as reagents for preparing compounds with more than one metal atom attached to the same carbon atom[15]

$$RC{\equiv}CH \xrightarrow[C_4H_8O]{B_2H_6} RCH_2CH(BH_2)_2 \xrightarrow{MeOH} RCH_2CH(B(OMe)_2)_2 \xrightarrow[NaOH]{HgCl_2} RCH_2CH(HgCl)_2$$

Diboryl compounds are not monomers, but are likely to be highly associated through hydrogen-bridge bonding. The triborylmethide ion $[C(BH_2)_3]^-$ is known in its lithium salt and its reactions have been studied.[16]

Boranes with two organic substituents are, as mentioned, normally dimeric and thus tetrasubstituted derivatives of B_2H_6; but steric demands arising from bulky substituents can give rise to monomeric compounds. The first example to be encountered was bis(2,3-dimethyl-2-butyl)borane $BH(CMe_2CHMe_2)_2$ (dihexylborane),[17] its monomeric nature being demonstrated by infrared, n.m.r. and molecular-weight studies. The likelihood that steric factors are responsible for the lack of dimerization is supported by the observation that the degree of dissociation of the dimeric thexylmonoalkylboranes $(BHRCMe_2CHMe_2)_2$ [R = alkyl] varies with the size of the group R.[17]

With trisubstituted boranes BRR′R″, on the other hand, the possibility of dimerization through hydrogen-bridge formation no longer exists, so that these compounds are inevitably monomeric (provided that the substituent groups contain no donors).

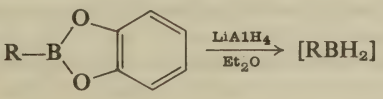
Generally speaking, even the fully substituted boranes are highly reactive and versatile compounds. Their chemistry is complex, as outlined below. They also have a wide application as catalysts and frequently will induce reactions. For example, triethylborane induces the reductive cleavage of tetrahydrofuran by lithium tri-*t*-butoxyaluminohydride $Li(t\text{-}BuO)_3AlH$.[18]

Monoalkylboranes

Apart from the question of dimerization (p. 400), the preparation of monoalkylboranes, even in solution, is rendered difficult on account of disproportionation. Accordingly they are best prepared—especially when required pure for synthetic purposes—in the presence of a satisfactory donor L.[19] The compound is then stabilized as $L.BHR_2$. Generally speaking, the most useful methods for preparing 'BH_2R' compounds *in situ* are (*a*) redistribution reactions (p. 89)

$$BR_3 + B_2H_6 \rightleftharpoons 3[BH_2R]$$

(*b*) reduction of alkylboronic acid derivatives[19]



and (*c*) hydroboration of terminal olefins (p. 103)

$$RCH{=}CH_2 \xrightarrow[C_4H_8O]{\frac{1}{2}B_2H_6} [RCH_2{-}CH_2BH_2]$$

Method (*a*) above has the disadvantage that it leads primarily to a mixture of products.

Dialkylboranes

Similar difficulties are associated with the preparation of the disubstituted 'BHR_2' compounds. Redistribution reactions and selected hydroboration reactions are applicable, as for the monosubstituted derivatives. An alternative approach is the action of lithium aluminium hydride on aryl diorganoborinates[20]

$$3R_2BOAr + LiAlH_4 \xrightarrow[0°C,\ 30\ min]{C_6H_{14}} 3[BHR_2] + LiAlH(OAr)_3$$

Again, the presence of a suitable donor allows stabilization as the adduct $L.BHR_2$.

Trialkylboranes

PREPARATION

The simplest trisubstituted organoboranes, the trialkylboranes BR_3, are readily prepared by a number of different methods. Most procedures depend on a boron trihalide or an ester of boric acid as starting material, as for the reactions with zinc dialkyls that led to the discovery of the trialkylboranes by Frankland over a century ago:[21, 22]

$$2B(OEt)_3 + 3ZnR_2 \rightarrow 2BR_3 + 3Zn(OEt)_2$$

$$2BCl_3 + 3ZnR_2 \rightarrow 2BR_3 + 3ZnCl_2$$

A Grignard reagent will serve instead of a zinc dialkyl, but if the reaction is being carried out in ethereal solution, it is advisable to avoid the use of BCl_3 (which noticeably cleaves ethers) and use BF_3 or its etherate instead.[23]

$$2BF_3 + 6PrMgCl \xrightarrow{Et_2O} 2BPr_3 + 3MgF_2 + 3MgCl_2$$

It has been shown that, contrary to earlier beliefs, the use of this reagent does not lead to isomerization.[24] Grignard reagents will also give organoboranes if they are prepared in the presence of diborane(6);[25, 26] here the organoboranes presumably arise via substituted diboranes which disproportionate. Alternatively, aluminium alkyls will serve as alkylating agents and moreover give superior yields, most conveniently with trialkyl borates: even though the reaction is very vigorous in its initial stages, it requires no solvent and has the further advantage that part of the boron (the theoretical rather than practical maximum is two-thirds) may be introduced in the form of anhydrous boric oxide.[27]

$$3AlR_3 + B_2O_3 + B(OR')_3 \rightarrow 3BR_3 + Al_2O_3 + Al(OR')_3$$

Certain other related methods have been compared[28] and their merits summarized.[29] In addition, alkyl aluminium halides have been used to provide the alkyl groups[30, 31] and a tetrafluoroborate to provide the boron:[31]

$$Me_3Al_2I_3 + B(OMe)_3 \xrightarrow[25°C]{no\ solvent} BMe_3 + Al_2(OMe)_3I_3$$

$$AlEt_3 + KBF_4 \rightarrow BEt_3 + KAlF_4$$

Resort can also be made to the hydroboration reaction (p. 103)

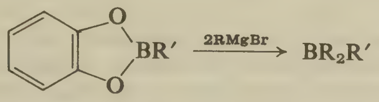
$$B_2H_6 + 6H_2C{=}CHR \rightarrow 2B(C_2H_4R)_3$$

to prepare trialkylboranes from diborane(6); but the reaction is in part reversible, so that as the number of carbon atoms in the alkyl group is increased beyond five, the product undergoes alkene elimination to an increasing extent when distilled under reduced pressure.[28] The preparation of more complex organoboranes has been reviewed recently.[32]

Some of the above methods can be adapted for preparing mixed substituted boranes of type BR_2R'. For example, exchange can be effected with a Grignard reagent incorporating a different organic substituent

$$BR_3 \xrightarrow[O(CH_2)_4]{R'MgCl} BR_2R'$$

This method has been used for the synthesis of dialkylcinnamylboranes.[33] Alternatively, organoboronic acid derivatives can be successfully alkylated by Grignard reagents[34]



But a convenient general method is to reduce a dialkylbromoborane with sodium hydride and allow the product to react with the appropriate alkene[35]

$$BR_2Br \xrightarrow{NaH} [BR_2H] \xrightarrow{alkene} BR_2R'$$

For alkylboranes of type $BRR'R''$ a method for calculating the numbers of different types of bonds has been applied to all possible isomers from BC_3H_9 to $BC_{10}H_{23}$.[36]

PROPERTIES

Physically, the lower members of the series of simple trialkylboranes BR_3 are all volatile and colourless substances: BMe_3 is a gas, b.p. −22°C, whereas BEt_3, $B(n\text{-}Pr)_3$ and $B(n\text{-}Bu)_3$ are liquids of low density. Trialkylboranes are immiscible with water, but are generally miscible with those organic solvents that are chemically inert towards them. Most is known about BMe_3, which has been studied by infrared,[37] Raman,[38] photoelectron,[39] far ultraviolet[39,40] and n.m.r. spectroscopy,[41] as well as by electron-impact techniques.[42] Molecular and physical properties for some tri-*n*-alkylboranes are listed in Table I. In addition, tables of thermodynamic data have been published for BMe_3,[53] BEt_3,[53] $B(n\text{-}Pr)_3$[52] and $B(n\text{-}Bu)_3$.[52] Several trialkylboranes with branched carbon chains have also been prepared. A comparison of values of the entropy of gaseous BMe_3 at 199·92 °K, obtained by calorimetry and by computation from spectroscopic data respectively, has demonstrated that the energy barrier to internal rotation of the methyl groups is small,[37,43,54] which points against any measure of π bonding in the B—C link. This conclusion is supported by modern theoretical treatments of the molecule,[55,56] which not only indicate the insignificance of π bonding, but make it appear likely that the B—C σ bond has an unexpectedly high degree of polarization with a pronounced positive charge on the boron atom; also that the carbon atom makes a greater *s* contribution to the B—C bond than to the C—H bonds.

*Table I.—Some Molecular and Physical Properties of the Lower Tri-*n*-alkylboranes*

Species	Ionization potential (eV)	r(B—C) (Å)	k(B—C) (mdyne $Å^{-1}$)	∠CBC	m.p. (°C)	b.p. (°C)	ΔHf (kcal mol^{-1})
BMe_3	9·69 (a) 10·01 ± 0·02 (i)	1·578 (b)	4·09 (c)	120° (b)	−161·5 (d)	−22 (e)	−34·1 (f,g,h)
BEt_3	9·66 (j,k)				−92·9 (d)	95 (d)	−44·9 (h)
$B(n\text{-}Pr)_3$					−65·5 (l)	156·1 (m,n)	−62·8 (h)
$B(n\text{-}Bu)_3$						209·7 (n)	−80·8 (h)

(*a*) Ref. 39. (*b*) Ref. 43. (*c*) Ref. 38. (*d*) Ref. 44. (*e*) Ref. 37. (*f*) Ref. 30. (*g*) Ref. 45. (*h*) Ref. 46. (*i*) Ref. 47. (*j*) Ref. 48. (*k*) Ref. 49. (*l*) Ref. 50. (*m*) Ref. 51. (*n*) Ref. 52.

Chemically, the trialkylboranes show a marked thermal stability in the absence of air, and are also stable under ordinary conditions towards water. However, even at room temperature and below, they react so rapidly with oxygen that the lower members of the series—at least as far as tripropylborane—are spontaneously inflammable in air and burn with a green flame. Higher members of the series, although they may not ignite spontaneously, nevertheless react quite rapidly with the atmosphere, producing fumes that have a characteristically sharp odour. The compounds must therefore be stored in sealed containers and regarded as a fire hazard.

ADDUCTS

Trialkylboranes form relatively stable adducts with many donors, especially with compounds of trivalent nitrogen and phosphorus, a property which they share with BH_3 itself. In general, however, the acceptor power is appreciably reduced by substitution at the boron. Thus the adduct of BMe_3 with the 5-membered ring donor tetramethylene phosphine $(CH_2)_4PH$ shows a measurable degree of dissociation at 50°C, whereas $(CH_2)_4PH.BH_3$ is still completely associated at 150°C.[57] Also, despite the complexes formed by BH_3 with $AsMe_3$ and $SbMe_3$, BMe_3 does not react with either at room temperature,[58] and shows only a very weak interaction with $AsMe_3$ at 0°C.[59] Neither, in contrast to BH_3, does BMe_3 form an adduct with PF_3. But trialkylboranes form quite firmly bound adducts with substituted amines and phosphines; and by means of displacement studies it has been shown—in spite of earlier suggestions to the contrary—that the order of base strength towards BEt_3 is the same as towards BH_3, namely $PMe_3 > NMe_3$[60] (cf. p. 26).

Adducts of organoboranes are prepared by simple addition, often at reduced temperatures. The ammonia complex $Me_3B.NH_3$ has long been known.[21] It is not spontaneously inflammable, and is a volatile crystalline solid of m.p. 56°C and b.p. 110°C. The vapour is virtually completely dissociated into BMe_3 and NH_3.[44, 61] In benzene or ether solution, however, the compound is not dissociated, and the solutions are stable towards air.[44] The Raman spectrum has been determined for both the liquid state and a solution in benzene.[62] The B—N stretching force constant is $2{\cdot}541 \pm 0{\cdot}112$ mdyne Å^{-1},[63] which is very much lower than the value for $H_3B.NH_3$ (4·45 mdyne Å^{-1} [64]). The heat of dissociation of the B—N bond, which is 13·75 kcal mol^{-1} for $Me_3B.NH_3$, does not vary monotonically as the nitrogen is progressively methylated (17·64, 19·26 and 17·62 kcal mol^{-1} for $Me_3B.NH_2Me$, $Me_3B.NHMe_2$ and $Me_3B.NMe_3$ respectively).[61] This trend does not correlate well either with trends in the chemical shifts for ^1H,[65] ^{11}B[65, 66] and ^{14}N[66] nuclei from n.m.r. studies or with the trend in the magneto-optical rotatory power.[67]

Structurally, not enough is known about these compounds. A microwave investigation of $Me_3B.NMe_3$[68] indicates a surprisingly long B—N bond (1·70–1·95 Å), but failure to observe the fine structure and lack of precise knowledge concerning the bond angles excluded a result of greater precision. On the other hand, the B—N stretching force constant of 3·157 mdyne Å^{-1} calculated from vibrational spectra[63] is distinctly on the high side for this class of compounds and would imply an intrinsically stronger and hence shorter bond. The comparatively low dissociation energy[61] is not necessarily evidence for a weaker and longer bond, since it is a net quantity which incorporates reorganization energies of the moieties on dissociation. N.m.r. studies with additional BMe_3 and NMe_3, respectively, show that $Me_3B.NMe_3$ is exchanging with these in solution by a dissociative mechanism with measured activation energies[69] quite close to the observed dissociation energy in the vapour phase.[61] Because of the rapid exchange, the importance of cooling BMe_3 adduct systems to a temperature at which the exchange process is slow on the n.m.r. time scale has been emphasized[69] and given as a reason for interpreting n.m.r. data from studies at ambient temperatures with caution. The results of several such studies in which $Me_3B.NMe_3$ is compared with related adducts have been published:[65, 70–73] in general they indicate that the acceptor strength of BMe_3 places it low on the scale of boron Lewis acids. Base displacement can occur, and probably normally takes place by a S_N1-B mechanism, as has been shown for displacement from $HPh_2B.NH_2Me$ by $NH_2CH_2CHPh_2$.[74] A theoretical study of $Me_3B.NMe_3$ by a CNDO/2 treatment has been carried out[75] and indicates that there is little charge on the B and N atoms, most of the charge being carried by the methyl groups: the calculated dipole moment is in reasonable agreement with the experimental value obtained from a solution in benzene (3·92 ± 0·03 D).[76] Trimethylborane also forms a slightly less strongly bound adduct with pyridine:[77] the heat of reaction to form $Me_3B.NC_5H_5$ is 15·27 kcal mol^{-1}, and slightly larger values are observed with 3-methyl- and 4-methylpyridines.[78] But, doubtless for steric reasons, with 2-methylpyridine the value drops to 9·95 kcal mol^{-1}, while no adduct is formed with 2,6-dimethylpyridine.[78] In general, however, the adducts formed by trialkylboranes with nitrogen compounds show appreciable stability, though with longer alkyl chains moderate heating may effect decomposition: thus the 1:1 adduct that tri-*n*-butylborane forms with piperidine eliminates 1-butene and hydrogen at 150°C to form N-di-*n*-butylborylpiperidine.[79]

The adducts of trialkylboranes with phosphines have received less study, but it has been shown that trimethylphosphine PMe_3 is a stronger base towards BMe_3 than PEt_3 or PVi_3, though, surprisingly, less strong than PMe_2Et.[80] The adduct $Me_3B.PMe_3$ melts at 118–121°C[81] and its heat of dissociation is 16·53 kcal mol^{-1}.[80] Its n.m.r. constants have been reported,[65] and (in common with $Me_3B.NMe_3$) it undergoes exchange reactions with excess of either the acidic or basic component by a dissociative mechanism.[60, 82, 83]

Complexes of trialkylboranes with ethers are exceedingly weak, and the components can normally be separated, even by vacuum fractionation at reduced temperatures. N.m.r. studies of trimethylborane-ether systems in dichloromethane at room temperature have shown that $Me_3B.OMeEt$ and $Me_3B.OEt_2$ are formed in sufficient concentration in solution to give a measurable signal,[70] in spite of the fact that $Me_3B.OMe_2$ could not be isolated, even at −78°C.[84] Both $Me_3B.SMe_2$ and $Me_3B.SeMe_2$ can be isolated as volatile white solids at the same temperature, at which the dissociation pressures are 1·25 and 8·6 Torr respectively, demonstrating the greater stability of $Me_3B.SMe_2$, which melts at −43 to −41°C: however, both compounds are fully dissociated in the vapour phase.[84] The sulphur compound has been investigated by n.m.r. spectroscopy.[70]

Very few adducts of trialkylboranes or other organoboranes with metal compounds are known, but mention must be made of the pale yellow solid σ-cyclopentadienylindium(I)-trimethylborane $(\sigma\text{-}C_5H_5)In.BMe_3$,[85] which contains an indium-boron bond. On the other hand, no iron-boron bond is formed when triphenylborane reacts with dicarbonyl-π-cyclopentadienyliron cyanide to give the nitrogen-linked adduct $(\pi\text{-}C_5H_5)Fe(CO)_2CN.BPh_3$.[86]

Neither are metal-boron bonds formed in the reaction of a trialkylborane with an alkali metal hydride or alkyl, which instead results in the formation of an ionic addition compound. Thus with NaH, trimethylborane gives sodium trimethylhydroborate(1−) $Na^+[BHMe_3]^-$; but NaH and LiH also give the adducts $NaH.2BMe_3$ and $LiH.2BMe_3$,[87] and the idea that these contain an ion with the singly bridged structure

$$[Me_3B{-}{-}H{-}{-}BMe_3]^-$$

finds support from infrared evidence.[88] In tetrahydrofuran or a polyether, temperature-dependent equilibria involving adduct anions are set up by tributylborane and $LiBH_4$ or $NaBH_4$.[89] With alkyls such as LiMe or LiEt, trimethylborane forms the compounds $LiBMe_4$[90] and $LiBMe_3Et$[91] respectively, which are stable towards dry air. However, these lithium salts have appreciable covalent character. They are soluble in solvents such as benzene and toluene, while $LiBMe_4$ melts at 189°C and can be sublimed in a vacuum at 140°C.[92] The structure of $LiBMe_4$ has been determined by X-ray crystallography and shown to be tetrameric in the solid phase.[92]

Trimethylborane will also react analogously with potassium germyl $KGeH_3$ at 0°C to produce the ion $[BMe_3(GeH_3)]^-$.[93] This ion apparently disproportionates rather readily according to the equation

$$2BMe_3(GeH_3)^- \rightarrow BHMe_3^- + BMe_3(Ge_2H_5)^-$$

These are rare examples of compounds containing a boron-germanium bond.

REACTIONS

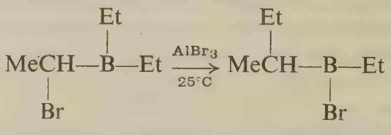
Apart from addition reactions discussed above, trialkylboranes (and organoboranes in general) undergo a very large number of other types of chemical reactions. Even though boron-carbon bonds are not so exceptionally reactive as boron-hydrogen bonds in electron-deficient surroundings, the organoboranes are nevertheless highly versatile in their chemical behaviour. Of the known types of reactions, upwards of thirty of them have already been shown to have use or potential use in synthetic organic chemistry, and further synthetic applications are still being discovered. This aspect has such extensive ramifications, that—in spite of its importance—its inclusion in the present treatise would not be practical or desirable, and the organic chemist is referred to extant summaries and reviews.[94–105] For technological applications, reference is also made to a book summarizing the patent literature for the period 1966–1972.[106] Many of the useful reactions of organoboranes proceed by free-radical paths.[107, 108]

Thermal Decomposition.—Pyrolysis of organoboranes may lead either to rearrangement or to general decomposition. The question of rearrangement is an additional highly complex feature of considerable synthetic importance. Rearrangements at the boron atom have been classified and reviewed,[109] but the very presence of a coordinatively unsatisfied boron atom in the vicinity may also promote rearrangement in the carbon chains. For aliphatic organoboranes with branched carbon chains, it has been claimed that thermal treatment at 120–200°C leads by isomerization mainly to *n*-alkyl groups and to some extent *i*-alkyl groups.[110] In general, no isomerization is observed at temperatures up to 100°C, but at higher temperatures the boron tends to migrate (contrathermodynamically!) along the carbon chains to the least sterically hindered position.

$$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH(BR}_2\text{)—CH}_2\text{—CH}_3 \xrightarrow[1\text{ h}]{160^\circ\text{C}} \text{CH}_3\text{—(CH}_2\text{)}_4\text{—CH}_2\text{BR}_2$$

It has been suggested that the mechanism depends on equilibria involving dehydroboration-hydroboration (p. 103), also termed olefin elimination-addition.[111–14] However, in certain cases the mechanism may be a somewhat different one.[115] At higher temperatures (200–300°C) irreversible pyrolysis sets in, resulting in methylboranes, boron heterocyclics and other products.[116] Polar solvents have an effect on the isomerization: for example, anisole and diphenyl ether promote isomerization at 160–180°C, but pyridine inhibits.[117]

With α-heterosubstituted organoboranes a different kind of isomerization can occur, especially when induced by an electrophile or nucleophile. Thus aluminium tribromide in carbon disulphide catalyzes the migration of an ethyl group of α-bromoethyldiethylborane[118]



$$\underset{\text{Br}}{\text{MeCH}}\text{—}\overset{\text{Et}}{\text{B}}\text{—Et} \xrightarrow[25^\circ\text{C}]{\text{AlBr}_3} \overset{\text{Et}}{\text{MeCH}}\text{—}\underset{\text{Br}}{\text{B}}\text{—Et}$$

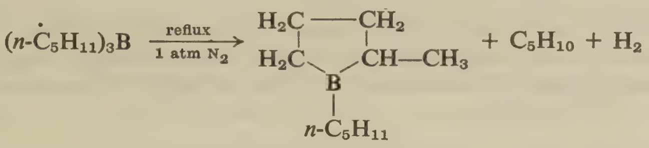
Similarly chloromethyldimethylborane, whose crystal structure is known,[119] undergoes a methyl shift in the presence of antimony pentachloride[120]

$$\text{BMe}_2\text{CH}_2\text{Cl} \xrightarrow[80^\circ\text{C}]{\text{SbCl}_5} \text{ClBMeEt}$$

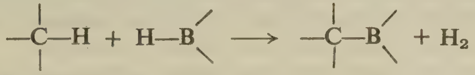
The presence of polar compounds can also instigate other types of change. Thus > 120°C dimethyl sulphoxide or anisole promotes the loss of one olefin molecule per molecule of trialkylborane, but benzaldehyde or furfural brings about the loss of two.[121] In the vapour phase, at least, the loss of olefin is a unimolecular process and, depending on the temperature, may proceed until three olefin molecules are lost: thus triisobutylborane is converted with the loss of C_2H_4 in three successive unimolecular steps of activation energy *c.* 30 kcal mol^{-1} to triethylborane[122]

$$(i\text{-Bu})_3\text{B} \xrightarrow{-\text{C}_2\text{H}_4} (i\text{-Bu})_2\text{BEt} \xrightarrow{-\text{C}_2\text{H}_4} i\text{-BuBEt}_2 \xrightarrow{-\text{C}_2\text{H}_4} \text{BEt}_3$$

The triethylborane produced may itself lose C_2H_4. When there are sufficient carbon atoms in the side chains, cyclization is often favoured. In such a case hydrogen is also eliminated, as with tri-*n*-amylborane,[123] which gives 1-*n*-amyl-2-methylborolane:



Under pressure in an autoclave tri-*n*-butylborane behaves in a corresponding manner.[124] Since alkene and not alkane separates, this may be taken as evidence that the decomposition occurs in two steps, the second being an example of an intramolecular hydrogen elimination. Intermolecular hydrogen eliminations of the type



are also not unknown, but are difficult to effect.[116]

With trimethylborane, unimolecular loss of olefin is not possible and a higher temperature is required to bring about decomposition. The pyrolysis of BMe_3 has been variously studied,[125–8] and the latest view of the principal product obtained at 450°C, a solid of m.p. 85°C, is that it is a cage compound of formula $(CH)_4(BMe)_6$. The (6 $^3P_1$) mercury-photosensitized decomposition of BEt_3 (alone and with added gases) has been studied and explained as the result of at least three competing primary processes that produce H_2, ethylene and ethyl radicals respectively.[129]

With Hydrogen and Hydrogen Compounds.—Reaction of trialkylboranes with hydrogen is difficult to realize, except in the presence of a catalyst. Thus, with hydrogen under pressure (54·5 atm), BBu_3 vapour over a Raney nickel catalyst at 100°C has been made to give butane plus a mixture of tri- and tetrabutyldiborane(6):[130]

$$2BBu_3 + 2H_2 \xrightarrow[\text{Raney Ni}]{100°C} 2BuH + B_2H_2Bu_4$$

Attempts to hydrogenate $Bu_3B.NHMe_2$, on the other hand, gave butenes instead of butane, plus $NHMe_2$ adducts of butyldiboranes, products that could arise from mere thermal decomposition.

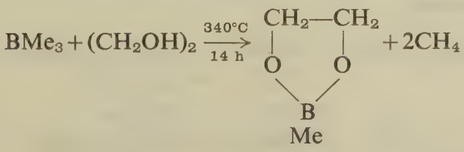
Protonolysis of BR_3 will also release the corresponding alkane RH, and can be effected by many active-hydrogen-containing compounds of oxygen, sulphur and nitrogen:[131–3]

$$BR_3 + H{-}X \rightarrow R_2B{-}X + RH \qquad [X = OR', OSO_2R', ON{=}CR'_2, SR', OC(O)R', NR'_2, NHR']$$

The temperature required by BMe_3 varies from room temperature to over 300°C, depending on the nature of the hydrogen-containing reactant,[134]

$$BMe_3 + H_2O \xrightarrow{c.\ 200°C} Me_2BOH + CH_4$$

$$BMe_3 + 2H_2O \xrightarrow{310°C} MeB(OH)_2 + 2CH_4$$



and even then only 1 or 2 methyl groups are detached from the boron atom. However, although aqueous mineral acids and alkalis do not affect trialkylboranes, carboxylic acids have considerable cleavage power and will in general remove two alkyl groups in the cold, and the third on heating in diglyme solution:[135]

$$BR_3 + 3EtCOOH \xrightarrow[\text{diglyme}]{\text{heat}} B(OC(O)Et)_3 + 3RH$$

Especially effective are tertiary carboxylic acids, which catalyze any of the above protonolysis reactions, so that temperatures above 100°C are not required: thus the addition of pivalic acid CMe_3COOH or one of its derivatives will effect the smooth and complete hydrolysis of trialkylboranes at room temperature.[136, 131]

Alkyl Transfer.—The direct transfer of alkyl groups from the boron to other elements is feasible. An extreme example of this is the exchange of alkyl groups of trialkylboranes with diethylberyllium:[137]

$$BR_3 + Be_2Et_4 \rightleftharpoons BEtR_2 + Be_2Et_3R$$

With $(n\text{-}Pr)_3B$, $(i\text{-}Bu)_3B$, $(Me_3CCH_2)_3B$ or $(Me_3SiCH_2)_3B$ full replacement is realizable on account of disproportionation of the mixed organoborane, but with $(s\text{-}Bu)_3B$ the crystalline compound Be_2Et_3H results with the loss of butene.

The wider use of metal salts and other metal compounds to effect alkyl-transfer reactions with organoboranes is known as *metallation* and has been reviewed.[138] It was discovered that mercuric salts or mercuric oxide would effect complete transference, not only in ethereal but also in alkaline aqueous media:[139, 140]

$$2BR_3 + 3HgCl_2 + 6NaOH \rightarrow 3HgR_2 + 2B(OH)_3 + 6NaCl$$

In ethers the transfer is to some extent reversible.[141, 142] In general, aryl groups are more readily transferred than primary alkyl groups, which in turn transfer more readily than secondary alkyl groups. Thus 2 of the 3 alkyl groups of a tri-*sec*-alkylborane are transferred with alkoxides of Hg(II) or Hg(I):[143, 144]

$$(s\text{-}R)_3B + 2Hg(OMe)_2 \rightarrow 2s\text{-}RHgOMe + s\text{-}RB(OMe)_2$$

$$(s\text{-}R)_3B + 2Hg_2(OR')_2 \rightarrow 2s\text{-}RHgOR' + 2Hg + s\text{-}RB(OR')_2$$

The use of the more easily available mercury(II) acetate brings no disadvantages,[145] and it is possible under relatively mild conditions to transfer all 3 of the groups of a tri-*n*-alkylborane to the mercury by a reaction which proceeds in stages:[146, 147]

$$(n\text{-}R)_3B + 3Hg(OAc)_2 \rightarrow 3n\text{-}RHgOAc + B(OAc)_3$$

$$(n\text{-}R)_3B + 3(n\text{-}R)HgOAc \rightarrow 3(n\text{-}R)_2Hg + B(OAc)_3$$

These reactions are favoured by the high affinity of boron for oxygen. Its still higher affinity for fluorine means that metal fluorides are generally more reactive than the other metal halides towards trialkylboranes. Thus reaction occurs between tri-*n*-butylborane and antimony trifluoride.[148] Probably an alkyl-transfer reaction proceeds according to the equation

$$3(n\text{-}Bu)_3B + SbF_3 \rightarrow 3(n\text{-}Bu)_2BF + (n\text{-}Bu)_3Sb$$

but at the temperature of the experiment (135–180°C) the tri-*n*-butylstibine decomposes and an antimony mirror results.

Silver compounds such as alkaline silver nitrate or silver oxide react differently from mercury(II) oxide and effect coupling of the alkyl groups.[149–51, 25] The products suggest that this occurs in two stages, the first being the formation of a very unstable silver alkyl, which has no more than a fleeting existence and decomposes by liberating radicals, most of which pair up. Thus, triethylborane produces mainly *n*-butane, with some ethane and ethylene:

$$BEt_3 + 1\tfrac{1}{2}Ag_2O + NaOH \xrightarrow{0^\circ C} 3AgEt + NaB(OH)_4$$

$$AgEt \longrightarrow Ag + C_2H_5\cdot$$

$$2C_2H_5\cdot \longrightarrow n\text{-}B_4H_{10}$$

$$2C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4$$

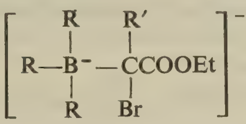
Gold(I) oxide Au_2O behaves similarly.

Organic groups may also be transferred from boron to carbon by reacting an organoborane in the presence of a tertiary alkoxide with an ester of an α-halogenosubstituted carbanion[152] or with an α-halogenosulphonyl compound:[153]

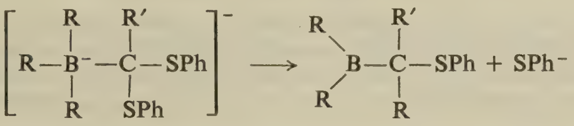
$$BR_3 + R'CHBrCOOEt + t\text{-}BuOK \xrightarrow[t\text{-}BuOH]{} R'CHROOEt + KBr + t\text{-}BuOBR_2$$

$$BR_3 + BrCH_2SO_2R' + t\text{-}BuOK \xrightarrow[t\text{-}BuOH]{} RCH_2SO_2R' + KBr + t\text{-}BuOBR_2$$

Similarly the di-α-substituted compound $R'CBr_2COOEt$ is converted to the diorgano-substituted derivative $R'CR_2COOEt$.[154, 155] These reactions probably involve intermediate adduct anions such as



which undergo an alkyl shift of type described above (p. 406). Other α-heterosubstituted adduct anions, such as those containing organothio groups, undergo similar alkyl shifts:[156]



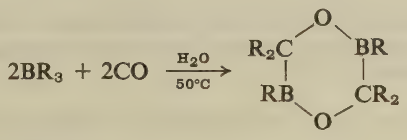
The function of organoboranes as alkylating and arylating agents and their application in syntheses has been reviewed.[157, 158]

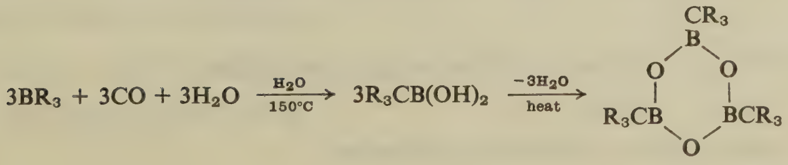
When the heteroatom is attached to a carbon chain at a point several atoms removed from the boron atom of a borane(3) derivative, the possibility of ring closure arises. This increases the stability, especially when the borane is fully substituted. Thus the compound $Bu_2B(CH_2)_4NR_2$ is stable only in the cyclically coordinated form, whereas compounds of the type $R'B(OH)(CH_2)_nNR_2$ exist as equilibrium mixtures of the open-chain and cyclic forms[159] (cf. p. 400).

Alkyl groups are not redistributed between trialkylboranes and fully substituted carbonium ions, even at high temperatures, so that apparently $BR_3\text{-}CR'_3{}^+$ equilibria do not arise.[160]

With Metals.—Little information is available concerning the reaction of trialkylboranes with metals. With alkali metals in liquid ammonia (or ethylamine) solvent, hydrogen is evolved, but the hydrogen comes from the solvent[161–3] and the product is a salt of type $M[Me_3BNH_2]$, though in ethylamine the reaction may be more complex. Triarylboranes behave differently (p. 421).

With Carbon Monoxide.—Trialkylboranes do not share with borane(3) the power of forming an isolable carbonyl with carbon monoxide. However, it is possible that such carbonyls play a role as short-lived intermediates in important carbonylation reactions of a varied nature, in which one or more alkyl shifts from boron to carbon occur, usually in the presence of a hydroxy compound such as water, an alcohol or a glycol:[164, 165]





The mechanism involved in the last reaction is probably

$$BR_3 + CO \rightarrow [R_3B.CO] \rightarrow [R_2BC(O)R] \rightarrow \tfrac{1}{2}(RBOCR_2)_2 \xrightarrow[150°C]{H_2O} R_3CB(OH)_2$$

The carbonylation reaction has particular synthetic potential for synthesizing not only tertiary alcohols, but also aldehydes and ketones.[94, 166–9]

With Organic Radicals and Free Ions.—The formation of boron-carbon bonds accompanies a number of the above reactions. Boron-carbon bonds may also be formed when trialkylboranes are attacked by alkyl radicals. Thus one way in which methyl radicals attack triethylborane is displacement:

$$Me\cdot + BEt_3 \rightarrow BMeEt_2 + Et\cdot$$

The activation energy has been measured as 5·20 kcal mol^{-1}.[170] Hydrogen abstraction occurs simultaneously:

$$Me\cdot + BEt_3 \rightarrow CH_4 + Et_2BC_2H_4\cdot$$

for which the experimental activation energy is higher, namely 7·78 kcal mol^{-1}.[170] It would be expected that hydrogen abstraction from BMe_3 proceeds less readily than with BEt_3; and, indeed, CD_3 radicals abstract hydrogen with an enhanced activation energy, namely 9·98 kcal mol^{-1}.[171] That for hydrogen abstraction by CF_3 radicals is 6·59 kcal mol^{-1}.[171]

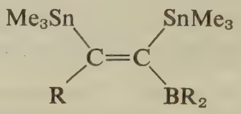
Ion cyclotron resonance spectroscopy has been used to determine the activation energies of reaction of BMe_3 with a number of free ions in the gas phase, including CH_5^+, $C_2H_5^+$ and CH_2OH^+.[47]

With Multiple Bonds.—Fully substituted organoboranes do not undergo a reaction comparable with the hydroboration reaction (p. 103 ff) with simple alkenes[111] or alkynes,[172] although partially substituted analogues BH_2R and BHR_2 will do so. For example, the reaction of the latter with alkynes[173]

$$BR_2H + R'C{\equiv}CH \rightarrow CHR'{=}CHBR_2$$

can be used for the synthesis of alkenes, dienes and enynes from alkynes and related compounds.[174] However, organoboration has exceptionally been observed to occur when the multiple bond is activated, as in bis(trimethylstannyl)acetylene:[175]

$$BR_3 + Me_3SnC{\equiv}CSnMe_3 \xrightarrow{25°C}$$

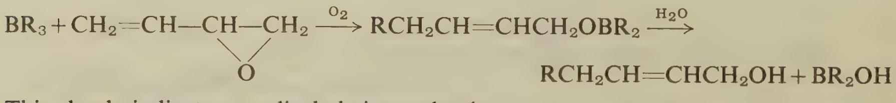


or when there is conjugation with a double bond to oxygen or nitrogen, in which case 1,4 addition occurs,[176] as exemplified by methyl vinyl ketone:[177]

$$BR_3 + CH_2{=}CHCMe{=}O \xrightarrow{25°C} CH_2RCH{=}CMeOBR_2$$

Such reactions also occur with imines and vinyl derivatives of ethylene oxide, but need to be induced: no reaction occurs in the absence of catalytic amounts of oxygen or other free-radical initiator:[178, 179]

$$BR_3 + CHMe{=}CHCH{=}NR' \xrightarrow{O_2} RCHMeCH{=}CHN(BR_2)R' \xrightarrow{MeOH} RCHMeCH_2CH{=}NR' + BR_2OMe$$



$$BR_3 + CH_2{=}CH{-}\underset{\diagdown O \diagup}{CH{-}CH_2} \xrightarrow{O_2} RCH_2CH{=}CHCH_2OBR_2 \xrightarrow{H_2O} RCH_2CH{=}CHCH_2OH + BR_2OH$$

This clearly indicates a radical-chain mechanism.

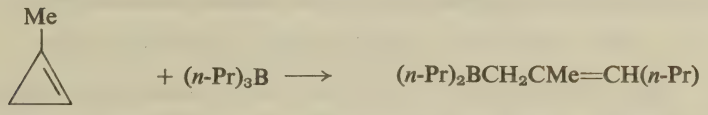
But organically trisubstituted boranes sometimes react with alkenes in other ways. The most obvious way is the displacement of an alkene by another less volatile alkene (transalkylation). Usually temperatures of 120°C or more are required.[111] Thus the sole product which remains from the reaction of 1-dodecene with tri-*n*-propylborane at temperatures $\leqslant 230°C$ is tri-1-dodecylborane:[180]

$$B(C_3H_7)_3 + 3C_{12}H_{24} \rightarrow B(C_{12}H_{25})_3 + 3C_3H_6$$

With styrene $PhCH{=}CH_2$ transalkylation occurs readily at 130°C.[115] Trialkylboranes can also bring about the isomerization of compounds containing double bonds, for example, of dimethyl-$\gamma\gamma$-dimethylallylamine:[79, 181, 182]

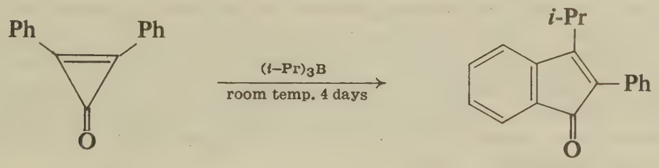
$$Me_2NCH_2CH{=}CMe_2 \xrightarrow[150°C,\ 15\ h]{BBu_3} Me_2NCH{=}CHCHMe_2$$

With cyclopropenes, trialkylboranes effect ring cleavage[183] or ring expansion[184]



1-methylcyclopropene

di-*n*-propyl(2-methylhex-2-en-1-yl)borane



diphenylcyclopropenone

3-isopropyl-2-phenyl-1-indenone

Vinyllithium derivatives, $LiRC{=}CH_2$, form ionic adducts with trialkylboranes that have synthetic potential:[185]

$$LiMeC{=}CH_2 \xrightarrow{BR_3} Li^+[Me(R_3\overset{(-)}{B})C{=}CH_2]^- \xrightarrow{I_2} \text{isopropenylalkanes}$$

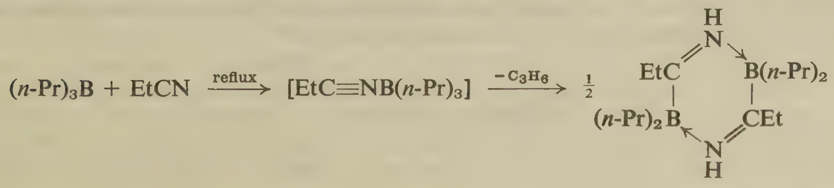
Alkynes can replace alkenes from trialkylboranes[172]

$$BEt_3 + 3RC{\equiv}CR \xrightarrow{150\text{–}70°C} B(CR{=}CHR)_3 + 3C_2H_4$$

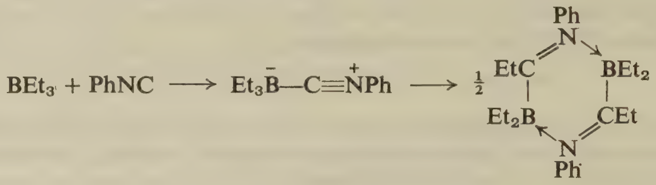
but, like vinyllithium compounds, ethynyllithium and ethynylsodium derivatives add on trialkylboranes to form reactive ionic products (trialkylalkynylborates):

$$MC{\equiv}CR' + BR_3 \rightarrow M^+[R_3\overset{(-)}{B}{-}C{\equiv}CR']^- \qquad [M = Li, Na]$$

which may be used as intermediates in the synthesis of a variety of products.[186–9] The reaction occurs slowly at room temperature or a little above, but a considerably higher temperature is required for an organic cyanide $R'C{\equiv}N$ to effect reaction.[190, 191] Although the first product is probably $R'C{\equiv}N.BR_3$, at the temperature required it eliminates alkene and undergoes cyclization.



Isocyanides, however, will react at room temperature in ether solution to give cyclic compounds, apparently via the isolable intermediate $R_3\overset{-}{B}—C\equiv\overset{+}{N}R'$:[191, 192]



In this case there is an alkyl transfer from boron to carbon.

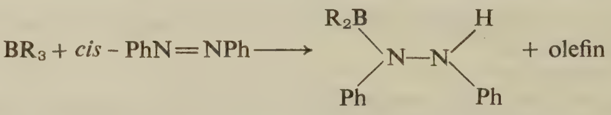
Boron-carbon bonds are also formed when trialkylboranes are reacted with ylides. For example, tri-*n*-hexylborane reacts at room temperature with triphenylarsonium benzylide $Ph_3\overset{+}{A}s\overset{-}{C}HPh$, although the first products have not been identified.[193] But the initial products from reactions with ylides of sulphur are known:[193–5]

$$BR_3 + Me_2\overset{+}{S}\overset{-}{C}H_2 \rightarrow [Me_2\overset{+}{S}CH_2\overset{-}{B}R_3] \rightarrow R_2BCH_2R + SMe_2$$

$$BR_3 + Me_2\overset{+}{S}(O)\overset{-}{C}H_2 \rightarrow [Me_2\overset{+}{S}(O)CH_2\overset{-}{B}R_3] \rightarrow R_2BCH_2R + Me_2SO$$

The action of nitrogen compounds on trialkylboranes is of considerable importance. Apart from the power of adduct formation already referred to (p. 404) and shared by compounds of trivalent phosphorus, primary and secondary amines are capable at higher temperatures of effecting protonolysis (p. 407), especially in the presence of a catalyst.[131] Organoboranes are aminated by chloramine or hydroxylamine-O-sulphonic acid:[196] the nitrogen atom attaches itself to a carbon atom, while the boron atom selects the more electronegative oxygen or halogen. Imines do not react with trialkylboranes except in some cases where the C=N bond is conjugated with a C=C bond, when 1,4 addition may occur[178] (p. 410).

Cis-azobenzene (but not the *trans* compound) also cleaves one of the B—C bonds,[197–8]



but, as shown in Fig. 1, *trans*-azodicarboxylates reacts by two competing reactions,[198]

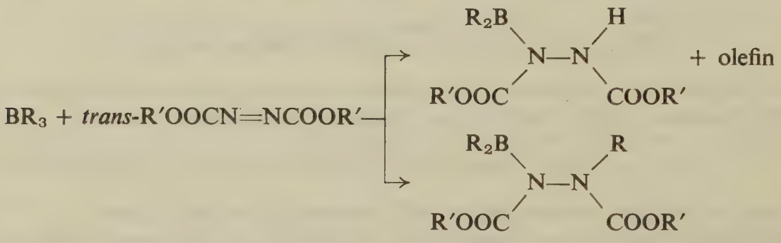
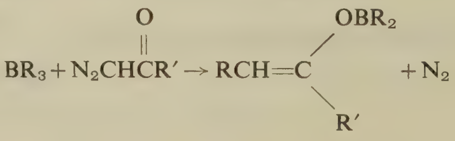


FIG. 1.—Competing reactions involved in the attack of a trialkylborane on a *trans*-azodicarboxylate

the second of which is a rare case of a homolytic alkylboration. Diazoketones and other diazo compounds also cleave trialkylboranes, but in this case neither fragment is attached to the nitrogen, which is released as a gas:[199–202]



Azides also react liberating two-thirds of their nitrogen to give a product readily hydrolyzed to a mixed secondary amine:[203, 204]

$$BR_3 + R'N_3 \xrightarrow[\text{(135°C)}]{\text{refluxing xylene}} R_2BNRR' + N_2$$

Nitric oxide reacts with tri-*n*-butylborane with B—C bond cleavage to give a mixture of at least three products.[205, 206] Boron-nitrogen and boron-oxygen bonds are formed.

With Oxygen and Oxygen Compounds.—The chemiluminescent reaction of BEt_3 with atomic oxygen has been studied.[207] With molecular oxygen reaction with organoboranes usually sets in well below room temperature, and spontaneous ignition in air may result. The reaction is a fast one, and under controlled conditions the oxygen molecule becomes inserted into a B—C bond:[107, 208–13]

$$BR_3 + O_2 \rightarrow R_2BOOR$$

However, the peroxy compound is not formed in a single step, but by a radical-chain mechanism. The reaction is first-order in $[BR_3]$ and in $[O_2]$, and the rate of primary initiation

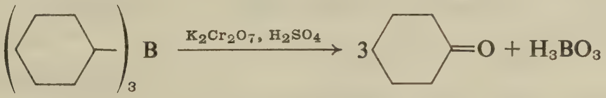
$$BR_3 + O_2 \rightarrow \cdot O_2BR_2 + R\cdot$$

is of the order of 10^{-3} mol^{-1} s^{-1}.[214]

Other oxidizing agents will oxidize organoboranes, for example, alkaline hydrogen peroxide:[215]

$$BR_3 + 3H_2O_2 + NaOH \rightarrow 3ROH + NaB(OH)_4$$

The oxidizing action of organic derivatives of hydrogen peroxide on BPr_3 has received special study.[216, 217] Again alcohols are the predominant products, but acidified dichromate leads to a ketone if the boron atom is linked to a secondary carbon atom, as with tricyclohexanylborane, which gives cyclohexanone.[96]



Oxidation by silver nitrate, however, leads largely to an interesting and useful coupling of the organic groups:[150]

$$BR_3 + 3AgNO_3 + 4KOH \rightarrow 3Ag + 3KNO_3 + KB(OH)_4 + 1\tfrac{1}{2}R\text{—}R$$

Typically the yields of bialkyls are in excess of 70 %, and biaryls can also be prepared in this way in slightly lower yields.[25, 98, 151] It has recently been discovered that electrolytic oxidation in alkaline methanol has the same effect.[218] The first steps at a platinum anode may be

$$BR_3 + OH^- \rightarrow BR_3OH^- \xrightarrow{-e} [BR_3OH] \rightarrow R\cdot + BR_2OH$$
$$R\cdot + \cdot R \rightarrow R_2$$

but at a graphite anode in the presence of a $NaClO_4$-MeOH mixture containing MeONa or of a MeCOOH-MeCOONa mixture, ethers and esters respectively are formed: it has been suggested that a carbonium-ion mechanism is involved.[219]

Non-oxidative reactions of trialkylboranes with oxygen compounds are less common than might be expected, and usually require either heating to above 100°C, catalysis or radical induction (where the reaction proceeds by a radical-chain mechanism). Thus trialkylboranes are normally stable towards water at 100°C, but pivalic acid and its derivatives (or, less efficiently, other carboxylic acids) catalyze hydrolysis at lower temperatures.[136] Indeed, it has been proposed that, in this way, catalyzed BEt_3 can be used to determine limited amounts of water by measuring the C_2H_6 evolved.[131] Alcoholysis can also be promoted by the same catalyst, while similar protonolysis reactions effected by hydroxyl-containing compounds as different as alkylsulphonic acids, N,N-dialkylhydroxylamines and oximes have received study from the point of view of catalysis and temperature.[131, 220] Most reactive towards trialkylboranes are the hydroxyl groups of carboxylic acids, which generally effect protonolysis at or near room temperature without a catalyst.

$$BR_3 + R'COOH \rightarrow BR_2OC(O)R' + RH$$

Ethers do not react with organoboranes, except possibly to give exceedingly weak addition complexes (p. 36). Except in the case of formaldehyde, the carbonyl group in aldehydes and ketones is also ordinarily inert, and reaction with trialkylboranes can only be effected by heating to about 150°C, when both reduction and enolysis compete with one another:[221]

$$BEt_3 + RCH_2C(O)R \left\{ \begin{array}{l} \rightarrow RCH_2CHROBEt_2 + C_2H_4 \\ \\ \rightarrow RCH{=}CROBEt_2 + C_2H_6 \end{array} \right.$$

(The latter mode of reaction is catalyzed by pivalic acid derivatives. Alternatively free radicals, including oxygen, may initiate reaction, as may light.) An exception arises if the C=O bond is conjugate with a C=C bond, when reaction by 1,4 addition may occur at more moderate temperatures[176] (p. 410). Formaldehyde is exceptional in reacting at 0°C

$$B(n\text{-}Bu)_3 + CH_2O \xrightarrow{0°C} (n\text{-}Bu)_2BOMe + 1\text{-}C_4H_8$$

but oxygen initiates an alternative free-radical reaction leading to a different product:[222]

$$B(n\text{-}Bu)_3 + CH_2O \xrightarrow{O_2} (n\text{-}Bu)_2BOCH_2(n\text{-}Bu)$$

The steps are believed to be:

$$BR_3 + O_2 \rightarrow R_2BO_2\cdot + R\cdot \qquad \text{(initiation)}$$

$$\left. \begin{array}{l} R\cdot + CH_2O \longrightarrow RCH_2O\cdot \\ RCH_2O\cdot + BR_3 \longrightarrow R_2BOCH_2R + R\cdot \end{array} \right\} \quad \textbf{(chain propagating)}$$

This is only one of many known examples which demonstrate the susceptibility of trialkylboranes to radical attack. Trialkylboranes are also susceptible to attack by excited molecules, as shown by the ultraviolet irradiation of mixtures with acetone or other ketones.[223, 224] Here the initiator of the chain reaction is an excited ketone molecule in the triplet state:

$$BR_3 + R^1R^2CO^* \rightarrow R^1R^2\dot{C}OBR_2 + R\cdot$$

For aromatic ketones, the rate constant of this initiation step has been shown to be of the order of 10^8 dm^3 mol^{-1} s^{-1} at 28°C.[225]

Trialkylboranes react readily with nitroso compounds, often at room temperature, eliminating one molecule of olefin:[197, 220]

$$(n\text{-}Bu)_3B + RN{=}O \rightarrow (n\text{-}Bu)_2BONHR + 1\text{-}C_4H_8$$

The boron here links itself to the oxygen. Although nitrobenzene is not reduced by diborane(6) under conditions so far tried (p. 117), under appropriate conditions, both $PhNO_2$ and *p*-chloronitrobenzene are reduced by tricyclohexylborane.[226] Reduction products included nitroso, azoxy, azo and N-substituted aniline compounds.

The kinetics and rate constants of alkoxyl and alkylperoxyl radicals with trialkylboranes[133, 227, 228, 210]

$$R'O\cdot + BR_3 \rightarrow BR_2OR' + R\cdot$$

$$R'OO\cdot + BR_3 \rightarrow BR_2OOR' + R\cdot$$

have been studied. They are very fast reactions with activation energies typically zero or < 5 kcal mol^{-1}.

With Sulphur Compounds.—The behaviour of trialkylboranes towards sulphur compounds has been much less studied. Reaction does not occur with thiols when pure at 150°C.[229] Initiation is however readily effected, and it has been shown that the ease of displacement in the reaction

$$BR_3 + BuSH \rightarrow BuSBR_2 + RH$$

follows the sequence primary-R < *sec*-R < *tert*-R.[230] The radical-chain mechanism involves attack by alkylthiyl radicals,

$$R'S\cdot + BR_3 \rightarrow R'SBR_2 + R\cdot$$

which, though fast, is not as fast as the above-mentioned attack by alkoxyl radicals.[133] This step is also involved in the oxygen-initiated reaction with organic disulphides.[231]

Trialkylboranes are converted to alkyl thiocyanates by ferric thiocyanate in aqueous tetrahydrofuran[232]

$$BR_3 + 6Fe(SCN)_3 + 3H_2O \xrightarrow{C_4H_8O} 3RSCN + B(OH)_3 + 6Fe(SCN)_2 + 3HSCN$$

The reaction of BMe_3 with the free ion H_3S^+ has been studied by means of ion cyclotron resonance spectroscopy and its activation energy determined.[47]

With Halogens and Halogen Compounds.—The reactions with halogens and halogen compounds have received more attention. Bromine in CH_2Cl_2 at room temperature[233, 234] and iodine on heating[235] cleave one B—C bond of a trialkylborane (but not very cleanly), the principal reaction following the equation

$$BR_3 + X_2 \rightarrow RX + BR_2X \qquad [X = Br, I]$$

The action of chlorine is inconveniently vigorous and destructive, but $FeCl_3$ provides a convenient source of chlorine which, in aqueous tetrahydrofuran, also leads to alkyl chlorides with the cleavage of all three B—C bonds[232]

$$BR_3 + 6FeCl_3 + 3H_2O \xrightarrow{C_4H_8O} 3RCl + B(OH)_3 + 6FeCl_2 + 3HCl$$

Similarly aqueous $CuBr_2$ can be used as a source of bromine to produce alkyl bromides.[236] However, bromine and iodine will also cleave more than one bond in base-induced reactions,[235, 237] and two of the three alkyl groups are converted to alkyl halide at room temperature:

$$BR_3 + 2I_2 + 2NaOH \rightarrow 2RI + 2NaI + BR(OH)_2$$
$$BR_3 + 3Br_2 + 4NaOH \rightarrow 2RBr + 4NaBr + B(OH)_3 + ROH$$

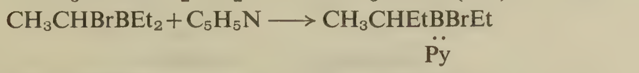
More recent studies have shown that in the iodine reaction, the NaOH can with advantage be replaced by NaOMe.[238] Also that in the absence of alkali and preferably in an inert solvent such as methylene dichloride, the significant step in the bromine reaction is not the cleavage of a B—C bond, but the α-bromination of a side-chain to give a product which reacts with the HBr formed:[239, 240]

$$B(CH_2R)_3 + Br\cdot \rightarrow R\dot{C}HB(CH_2R)_2 + HBr$$
$$R\dot{C}HB(CH_2R)_2 + Br_2 \rightarrow RCHBrB(CH_2R)_2 + Br\cdot$$
$$RCHBrB(CH_2R)_2 + HBr \rightarrow RCH_2Br + B(CH_2R)_2Br$$

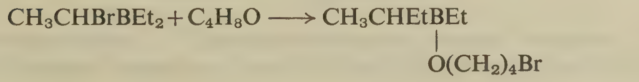
Thus here again there is a radical-chain mechanism. Initiation is facilitated by light. The α-brominated intermediate is capable of isolation if the HBr is removed as soon as it is formed. It undergoes an interesting rearrangement involving the migration of an alkyl group from boron to carbon on heating or treatment with certain other compounds:[241]

$$CH_3CHBrBEt_2 \xrightarrow[5\ h]{heat} CH_3CHEtBBrEt$$

$$CH_3CHBrBEt_2 + H_2O \xrightarrow{CH_2Cl_2} CH_3CHEtB(OH)Et + HBr$$



$$CH_3CHBrBEt_2 + C_5H_5N \longrightarrow CH_3CHEt\underset{\underset{Py}{\vdots}}{B}BrEt$$



$$CH_3CHBrBEt_2 + C_4H_8O \longrightarrow CH_3CHEt\underset{\underset{O(CH_2)_4Br}{|}}{B}Et$$

The production of *sec*-butyl groups from ethyl groups is of considerable synthetic significance,[242] and leads, for example, to a simple procedure for producing highly substituted alcohols.[243] A comparable α-iodination of BEt_3 does not seem to occur, but it has been shown that iodination to BEt_2I also proceeds by a radical mechanism,[244, 245] and the photochemical iodination has been quantitatively studied.[246] Hydrogen halides also cleave a B—C bond of trialkylboranes:

$$BR_3 + HBr \rightarrow R_2BBr + RH$$

From a study of the photochemically induced reaction of CCl_3Br with BEt_3, it has been shown that trichloromethyl radicals attack the borane in a side chain at the α position:[247]

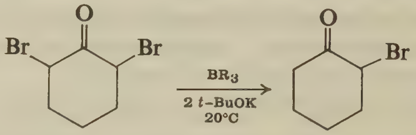
$$BEt_3 + \cdot CCl_3 \rightarrow CHCl_3 + CH_3CHBEt_2$$

and set up a radical chain with the production of $CH_3CHBrBEt_2$. Tri-*n*-butylborane reacts with CHF_2Cl in the presence of tetrahydrofuran and lithium triethylcarboxide to give an unidentified product which oxidizes to tri-*n*-butylcarbinol:[248]

$$(n\text{-Bu})_3B + HCF_2Cl \xrightarrow[65°C,\ 1\ h]{C_4H_8O\ LiOCEt_3} [\text{product}] \xrightarrow{[O]} (n\text{-Bu})_3COH$$

This procedure is better than the carbonylation reaction (p. 409), which gives the same product.

Trialkylboranes debrominate α,α'-dibromoketones in the presence of an alkali metal alkoxide:[249]

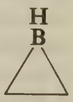


Dehalogenation of organic hypochlorites also occurs, but the boron becomes attached to the oxygen:[250]

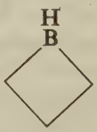
$$BR_3 + t\text{-BuOCl} \rightarrow t\text{-BuOBR}_2 + RCl$$

Cyclic Organoboranes

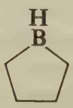
Cyclic organoboranes of formula $HB(CH_2)_n$, some of which have been characterized, are, as would be expected, dimeric through hydrogen bridge bonding. Hence they are true derivatives of B_2H_6 and are frequently collectively termed bis-boracyclanes. Nevertheless, the hypothetical monomeric boretane $HB(CH_2)_3$ has been treated theoretically.[251] On the other hand, B-substituted derivatives of these compounds are normally monomeric and hence substituted derivatives of BH_3. Their nomenclature is based on the following generic names:



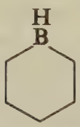
borirane



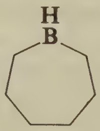
boretane



borolane



borinane



borepane

Reported examples include 1-ethynyloxyborirane,[252] 1-ethyl-3-methylborolane,[253] 1-*n*-hexyl-3,5-dimethylborinane[254] and 1-*n*-hexyl-3,6-dimethylborepane.[254]

Unsaturated Aliphatic Organoboranes

Since hydridic B—H bonds hydroborate C=C and C≡C bonds, mono- and disubstituted boranes containing unsaturated aliphatic substituents cannot be prepared. The trisubstituted derivatives, such as trivinyl- and triallyborane are readily preparable, however, and owe their existence to the fact that fully substituted boranes do not ordinarily enter into a reaction with multiple bonds comparable to that of hydroboration. These compounds cannot be prepared from B_2H_6, which attacks unsaturated groups, but require other starting materials.

Trivinylborane was first prepared from vinylsodium according to the reaction[255,256]

$$BMe_2Br + NaVi \rightarrow NaBr + BMe_2Vi$$

the first product BMe_2Vi disproportionating in steps to $BMeVi_2$ and BVi_3 plus BMe_3. However, relative to the trialkylboranes, the purified products show an unusual stability with respect to disproportionation. Other methods of preparing trivinylborane are available, including the interaction of $PbVi_4$ and BCl_3,[257] while substituted-vinyl analogues may also be prepared by the controlled monohydroboration of internal acetylenes[258]

$$12RC{\equiv}CR + 3NaBH_4 + 4BF_3 \rightarrow 4B(RC{=}CHR)_3 + 3NaBF_4$$

$$RC{\equiv}CR + BHR'_2 \rightarrow R'_2BCR{=}CHR$$

Addition to the triple bond is *cis*.

The simplest member of the series, BVi_3, is a volatile liquid with a boiling point (extrapolated) of 55°C.[256] It has been studied from the point of view of its vibrational,[259,260] ultraviolet,[261] n.m.r.[261,262] and photoelectron[263] spectra, and its structure has been determined by electron-diffraction investigation.[264] The molecule is apparently planar, steric strain being reduced by some distortion of the vinyl groups. The question of whether the B—C bonds are strengthened by π bonding has been discussed;[102,263,265] the latest evidence from bond lengths[264] indicates that a measure of π bonding occurs. This is supported by the strong deshielding of the β carbon atom observed in the ^{13}C n.m.r. spectra of α,β-unsaturated alkenylboranes.[266,267] Theoretical treatments of BVi_3 have been undertaken by LCAO-MO-SCF,[268] CNDO/S,[269] STO-3G-SCF,[270] INDO[271,272] and VESCF[272] methods. Though the organic chemistry of trivinylborane has been little studied, it is probably largely predictable: for example, it undergoes the usual coupling reaction with silver nitrate,[273] and is capable of entering into adduct formation with several Lewis bases, which is accompanied by a broadening of the vinyl region in the ^{1}H n.m.r. spectra.[274] It also condenses with B_2H_6 to give a liquid product of low volatility and with higher boranes to give glassy solids.[275] However, it cleaves the boron-boron bond of B_2F_4 and B_2Cl_4:[276]

$$BVi_3 + B_2X_4 \rightarrow Vi_2BCH(BX_2)CH_2BX_2 \qquad [X = F, Cl]$$

Many vinylboranes containing other ligands are known, and among those which have been structurally studied by microwave spectroscopy is $BViF_2$.[277] Boranes containing organically substituted vinyl groups may be prepared from trialkylboranes and ethynyllithium:[189]

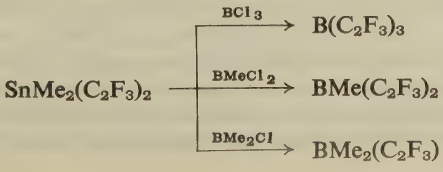
$$BR_3 + LiC{\equiv}CH \rightarrow Li^+[R_3\overset{(-)}{B}C{\equiv}CH]^-$$

$$Li[R_3BC{\equiv}CH] + HCl \rightarrow LiCl + R_2BCR{=}CH_2$$

In addition, boranes containing inorganically substituted vinyl groups have been characterized. These include species with organosilicon-substituted vinyl groups prepared *via* an adduct of ethynylsodium:[278]

$$Na[R_3BC{\equiv}CH] + Me_3SiCl \rightarrow NaCl + R_2BCR{=}CMeSiMe_3$$

and species with perfluorovinyl groups such as $B(C_2F_3)_3$ (b.p. 104·9°C),[279] $BMe(C_2F_3)_2$ (b.p. 93°C)[280] and $BMe_2(C_2F_3)$ (b.p. 33°C)[280] prepared from dimethylbis(perfluorovinyl)tin:



Various vinyl and substituted-vinyl compounds of boron have been investigated by n.m.r. spectroscopy and their J_{BH} values estimated indirectly.[262, 281, 282]

Allyl derivatives of borane(3) are also well known, and have been the subject of intensive study, more especially in Russia. Triallylborane $B(C_3H_5)_3$ can be prepared in good yield from BF_3, its etherate or a borate ester and allylmagnesium bromide[283] or allylaluminium sesquibromide[284]

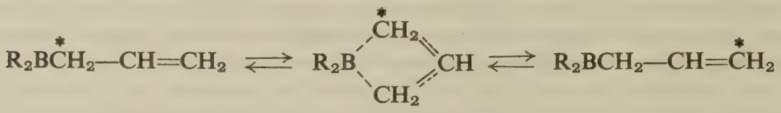
$$(C_3H_5)_3Al_2Br_3 + B(OR)_3 \rightarrow \underset{(80\%)}{B(C_3H_5)_3} + AlBr_3 + Al(OR)_3$$

It boils at 153·5–154°C at 720 Torr. Mixed allylboranes can sometimes be conveniently prepared by hydroborating the appropriate allenic hydrocarbon with an alkyldiborane, e.g.[285]

$$Me_2C{=}C{=}CH_2 + \tfrac{1}{2}B_2H_2Et_4 \rightarrow \underset{(90\%)}{Me_2C{=}CH{-}CH_2BEt_2}$$

(Some isomeric material is however formed at the same time.) The physical properties of a number of mixed allylboranes and substituted allylboranes have been tabulated.[286]

Chemically the allylboranes exhibit a higher reactivity than trialkylboranes, especially towards nucleophilic reagents containing labile hydrogen. This enhanced reactivity is accompanied by an easier cleavage of the boron-carbon bond. Many allylboranes, including $B({-}CH_2{-}CH{=}CH_2)_3$, undergo an allyl rearrangement in which carbon atoms change their positions in the chain, as has been demonstrated by n.m.r. studies. For an explanation, the assumption of a transition state is required:



These and numerous other types of reactions entered into by allylboranes have been reviewed.[286, 287] Especially noteworthy is the reaction with vanadium tetrachloride[288]

$$B(C_3H_5)_3 + 3VCl_4 \rightarrow BCl_3 + 3C_3H_5VCl_3$$

More recently it has been shown that compounds containing C=N and C≡N bonds react with triallylborane, which adds across the multiple bond with the boron attaching itself to the nitrogen,[289] e.g. for methacrylonitrile,

$$CH_2{=}CMeC{\equiv}N + B(C_3H_5)_3 \rightarrow CH_2{=}CMeC(C_3H_5){=}NB(C_3H_5)_2$$

Also that in exchange with $B(OR)_3$, $B(SR)_3$, BCl_3 or BBr_3, triallylborane reacts with accompanying rearrangement of the allyl group.[290, 291] The latest evidence from ^1H, ^{11}B and ^{13}C n.m.r. studies indicates that σ bonding between the boron and allyl group is retained in allyl rearrangements of triallylborane.[292]

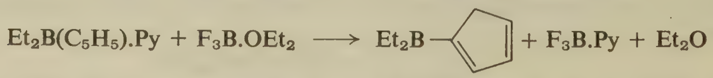
The allenylborane $R_2B{-}CR{=}C{=}CH_2$ [R = cyclopentyl] has been prepared from the interaction of the lithium salt of propargyl chloride and tricyclopentylborane[293]

$$BR_3 + LiC{\equiv}CCH_2Cl \dashrightarrow LiCl + R_2BCR{=}C{=}CH_2$$

The structure has been demonstrated by n.m.r. studies and by its conversion to the deuterated allenic hydrocarbon $DRC{=}C{=}CH_2$ on treatment with MeCOOD.

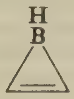
The cyclopentadienylborane $Et_2B(C_5H_5)$ has been prepared by treating the trimethylamine or pyridine adduct of Et_2BCl successively with cyclopentadienylsodium and boron trifluoride:[294, 295]

$$Et_2B(Cl).Py + NaC_5H_5 \rightarrow NaCl + Et_2B(C_5H_5).Py$$

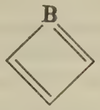


The n.m.r. spectrum is only compatible with a structure in which the boron is linked by a σ bond to an unsaturated carbon atom that is simultaneously linked to a CH_2 group in the C_5 ring. The compound dimerizes slowly at room temperature and more rapidly on heating or in the presence of a Lewis acid, when a Diels-Alder reaction is involved. It forms a yellow crystalline 1:1 addition compound (m.p. 140°C) with sodium, while with $FeCl_2$ it forms ferrocene $Fe(\pi\text{-}C_5H_5)_2$. An analogous (methylcyclopentadienyl)borane $Et_2B(C_5H_4Me)$ has been similarly prepared:[295] in this compound the CH_2 group is preserved and the methyl group is linked as far from the boron atom as possible to carbon atom 3 or 4.

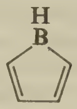
The possibility of forming cyclic unsaturated boranes in which the boron is incorporated into the ring arises. The nomenclature adopted in such cases is the following:



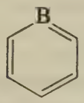
1H-borirene



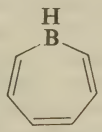
borete



1H-borole

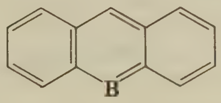


borin

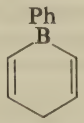


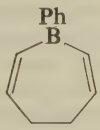
1H-borepin

The unsubstituted compounds have so far defied preparation. The alternate members of this sequence with hydrogen attached to the boron would be expected to dimerize by means of hydrogen-bridge bonding and so form derivatives of diborane(6). Nevertheless the hypothetical monomeric 1H-borirene[296] has received a theoretical study leading to the conclusion that considerable electron delocalization occurs. The ring should therefore have a degree of aromatic (or antiaromatic!) character, and this would also be expected for the compounds with 4-, 5-, 6- and 7-membered rings. Attempts to prepare borete derivatives have failed or possibly resulted in a cationic form, but there is a claim to have prepared the neutral borin derivative 9-boraanthracene



as an adduct with SMe_2.[297] In contrast to unsubstituted 1H-borirene, 1H-borole and 1H-borepin, their B-substituted derivatives would, predictably, be monomers; poorly characterized examples have been reported, including the unsubstantiated pentaphenylborole[298] and heptaphenylborepin.[299] The 1-alkylborirenes[272, 296] and 1-alkylboroles[296] have also been examined from a theoretical standpoint. The preparation of such compounds is confronted by considerable difficulty, but an attempt has been made to study the effect of unsaturation on cycloboranes.[300] A number of less unsaturated cyclic boranes have been more readily prepared, such as 1-phenyl-1,4-dihydroborin[301] and 1-phenyl-1-boracyclohepta-2,6-diene:[300]





The probable conclusions to be drawn on the limited evidence available, is that boron at most only very unreadily enters into aromatic bonding, and that more work needs to be done on such of the compounds as have been—usually all too briefly—reported, before any of the claims to have prepared them can be unreservedly accepted.

Triethynylborane $B(C{\equiv}CH)_3$ cannot be isolated at room temperature, although there is evidence that it is formed in solution at −60°C from the interaction of ethynylsodium $NaC{\equiv}CH$ with BF_3, BCl_3 or $B(OMe)_3$.[302] On warming to −30°C, however, a vigorous reaction sets in accompanied by a change in colour. Alkylated and arylated derivatives of $B(C{\equiv}CH)_3$ behave similarly before reaching room temperature. Nevertheless, adducts can be prepared that are stable towards air, shock, and a fair degree of heating. For example, the pyridine complex $(HC_2)_3B.NC_5H_5$ is a light-brown crystalline solid of m.p. 153°C that can be sublimed easily. Such adducts can also be formed from adducts of dialkylalkynylboranes, which undergo a kind of disproportionation reaction on heating with trimethylamine N-oxide:[303]

$$3Et_2B(C{\equiv}CMe).NMe_3 + 6Me_3NO \rightarrow B(C{\equiv}CMe)_3.NMe_3 + 2B(OEt)_3 + 8NMe_3$$

Alkyldi-1-alkynylboranes $RB(C{\equiv}CR')_2$ can only exceptionally be isolated from their pyridinates,[303] but dialkyl- and diaryl-alkynylboranes are more readily obtained in good yield by this method. Even so, they decompose rather readily. These compounds, including the unsubstituted ethynyl compounds, may be prepared by reactions of the type[303–5]

$$M{-}C{\equiv}C{-}R' + R_2BX \rightarrow MX + R_2B{-}C{\equiv}CR'$$
$$[M = Li, Na, MgX;\ X = \text{halogen};\ R' = H, \text{alkyl, aryl}]$$

Use of the reagent $BrMg{-}C{\equiv}C{-}MgBr$ instead of $BrMg{-}C{\equiv}CR'$ leads to the related and moderately stable bis(dialkylboryl)acetylenes, $R_2B{-}C{\equiv}C{-}BR_2$.[306] Bis(dialkylamino)alkynylboranes $(R_2N)_2B{-}C{\equiv}CR'$ and dialkoxyalkynylboranes $(RO)_2B{-}C{\equiv}CR'$ are preparable by comparable methods[304] and are more stable than dialkylalkynylboranes, the lower homologues being distillable without decomposition. Diethylamino-bis(propynyl)borane reacts with dimethylstannane or phenylphosphine to give respectively a 1-bora-4-stanna-cyclohexa-2,5-diene[307] or a 1-bora-4-phospha-cyclohexa-2,5-diene derivative,[308] as shown in Fig. 2.

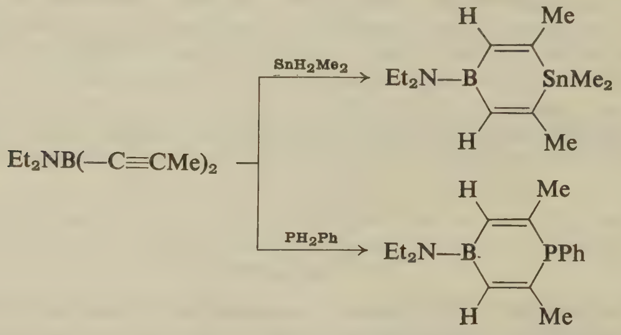


FIG. 2.—Formation of heterocyclic boranes in the reactions of diethylamino-bis(propynyl)-borane(3) with dimethylstannane and phenylphosphine respectively

The possibilities of synthesizing aliphatic organoboranes containing heteroatoms in the side chain are enormously large, and compounds of type BH_2CH_2Y [$Y = Li$, HBe, NH_2, OH, F] have received theoretical treatment.[14] However, relatively few compounds with substituted side chains have been prepared to date. One worth mentioning is the silicon-containing compound $B(CH_2SiMe_2OSiMe_3)_3$,[309] which has recently been regarded as a possible source of 1-silaethylene intermediates.[310] Donor atoms such as nitrogen or sulphur in the side chain at a suitable distance from the boron atom may lead to internal coordination (p. 400). We have already seen (p. 406) that halogen atoms such as bromine in the α-position of a side chain readily migrate, and this is also true of fluorine atoms, even when in the β position.[311] Because of this, and the tendency of CF_3 groups when attached to boron to split off difluorocarbene CF_2—which commonly appears as a solid polymer—attempts to prepare fluorinated organoboranes for a long time met with little success.[312] However $B(CH_2F)F_2$ (b.p. 7°C)[313] and $B(CF_3)F_2$[314, 315] have been prepared as follows:

$$BF_3 + CH_2N_2 \xrightarrow{-40^\circ C} B(CH_2F)F_2 + N_2$$
$$KB(n\text{-}Bu)_2 + CF_3I \xrightarrow{25^\circ C} KI + B(n\text{-}Bu)_2CF_3$$
$$B(n\text{-}Bu)_2CF_3 + BF_3 \longrightarrow B(CF_3)F_2 + B(n\text{-}Bu)_2F$$

Although both compounds are monomeric in the vapour, the former, at least, is associated in the liquid phase through interaction between the carbon-bonded fluorine and the boron of a second molecule. Both compounds can be stored *in vacuo*, but otherwise show restricted stability and readily undergo catalytic decomposition.

In contrast to fluorine in the α or β position, fluorine in the γ position of a side chain attached to boron is stable and does not migrate at 100°C. Thus it is possible to prepare $BMe_2(CH_2CH_2CF_3)$[311] along with its isomer $BMe_2(CHMeCF_3)$:

$$\tfrac{1}{2}B_2H_2Me_4 + CH_2{=}CHCF_3 \rightarrow BMe_2(CH_2CH_2CF_3)$$

Perfluorovinylboranes containing the —C_2F_3 group (p. 417) have also been prepared, and that by the action of chloroboranes on $SnMe_2(C_2F_3)_2$.[262,279,280] Here the formation of a B—F bond by the simple fission of CF_2 is not possible, and because migration of the fluorine also does not occur these compounds show greater stability. Thus $BMe_2(C_2F_3)$ and $BMe(C_2F_3)_2$ are stable at 100°C and also show a surprising resistance to disproportionation.[280] They are however hydrolyzed at 120°C with the production of C_2HF_3.

Arylboranes

Many arylboranes have been characterized. Triphenylborane BPh_3 is a comparatively stable compound that can be prepared by many of the general methods used for preparing trialkylboranes. Recommended methods include the treating of PhMgBr with $BF_3.OEt_2$[316] and the thermal decomposition of $[NHMe_3][BPh_4]$ prepared from LiPh and $Cl_3B.OEt_2$:[317,318]

$$4LiPh + Cl_3B.OEt_2 \xrightarrow{Et_2O} LiBPh_4 + 3LiCl + Et_2O$$

$$LiBPh_4 + NHMe_3Cl \xrightarrow{Et_2O} [NHMe_3][BPh_4] + LiCl$$

$$[NHMe_3][BPh_4] \xrightarrow{heat} BPh_3 + NMe_3 + C_6H_6$$

Triphenylborane is a solid of m.p. 142°C. In the crystal the phenyl groups are tilted approximately 30° with respect to the valence plane of the boron atoms in a propeller-like arrangement, and, otherwise than for $GaPh_3$, there are no intermolecular interactions.[319,320] The enthalpies of sublimation[321] and formation at 25°C[322] are $26{\cdot}6 \pm 0{\cdot}3$ and $11{\cdot}6 \pm 1{\cdot}9$ kcal mol^{-1}, corresponding to a B—C bond energy in BPh_3 of 109·7 kcal mol^{-1}, more than 20 kcal mol^{-1} stronger than that in trialkylboranes. Decomposition sets in above 316°C.[323]

Chemically triphenylborane and triarylboranes are very sensitive to atmospheric oxidation. Though they have been less well studied than the trialkylboranes, their chemistry is in general similar, even if their reactions tend to be less vigorous or comparatively sluggish. Worthy of mention is that some triarylboranes are cleaved at room temperature by alkali metals, while others are not.[324] Where reaction occurs, either the arene or biaryl result. In all cases, however, e.s.r. studies have shown that the radical anion BAr_3^- is formed. Tri-1-naphthylborane reacts differently to give the nearly black disodium salt $Na_2B(C_{10}H_7)_3$.[325–7] It has been noted that tribenzylborane undergoes an allyl-type rearrangement (p. 418) during reactions with acetylenes.[328–30]

Of the numerous substituted arylboranes, mention should be made here of the fully fluorinated compound tris(pentafluorophenyl)borane $B(C_6F_5)_3$.[71,331] It is prepared in good yield from the reaction

$$BCl_3 + 3LiC_6F_5 \xrightarrow[-20°C]{C_5H_{12}} B(C_6F_5)_3 + 3LiCl$$

as a white solid that is sublimable *in vacuo* at 80°C and unexpectedly stable thermally, but decomposes slowly at 210°C. It does not react with air or even with oxgyen at 150°C. The compound possesses strong acceptor properties towards Lewis bases, while with excess LiC_6F_5 it forms the salt $Li[B(C_6F_5)_4]$.

DERIVATIVES WITH SILICON SUBSTITUENTS

We are here concerned only with borane(3) derivatives that contain a B—Si bond, and very few of these have been studied. Thus silyl compounds containing the —SiH_3

group directly linked to the boron of a monoborane have been characterized only in the cases of $H_3SiBH_2.NEt_3$, $H_3SiB(NMe_2)_2$, $H_3SiB(NEt_2)_2$ and $H_3SiB(Bu)NMe_2$.[332] Their preparation is effected by the action of silylpotassium on a chloroborane, e.g.

$$SiH_3K + ClB(NR_2)_2 \rightarrow H_3SiB(NR_2)_2 + KCl$$

The compounds are colourless and volatile in high vacuum, and are very sensitive towards moisture and oxygen. They decompose slowly at room temperature.

Substituted silyl derivatives of type $(Me_3Si)_{3-n}B(NR_2)_n$ and $(Ph_3Si)_{3-n}B(NR_2)_n$ are also known[333, 334] and are somewhat more stable. In addition, there are reports of fully halogenated silyl- and disilylboranes, including $F_2BSi_2F_5$[335] and Cl_2BSiCl_3.[336] Such compounds hydrolyze with vigour.

DERIVATIVES WITH GERMANIUM SUBSTITUENTS

The germyl compound $H_3GeB(NMe_2)_2$, which contains a B—Ge bond, is so far the only germanium-substituted borane to have been reported. It is very similar to the silyl analogue referred to above, but has an even more restricted stability. The preparation was analogously accomplished from GeH_3K.[337]

DERIVATIVES WITH TIN SUBSTITUENTS

Trialkylstannylboranes containing a B—Sn bond have been prepared in a like manner to the above-mentioned trialkylsilyl derivatives, but starting from the appropriate lithium compound R_3SnLi. The first to be prepared were $Et_3SnB(NMe_2)_2$, $Et_3SnB(NMe_2)Cl$ and $(Et_3Sn)_2BNMe_2$.[338] These compounds are rapidly hydrolyzed to boric acid and other products. At about 100°C $Et_3SnB(NMe_2)_2$ undergoes thermal decomposition into the diborane(4) derivative $B_2(NMe_2)_4$ and Sn_2Et_6. Methylchlorostannanes $SnMe_nCl_{4-n}$ have also been used to produce stannylboranes of formula $Me_nSn(BPh_2)_{4-n}$ [$n=0, 1, 2, 3$].[339, 340] In this case the boron is introduced by means of the compound bis(tetraphenyldiphosphinoethane)bis(diphenylboryl)cobalt:

$$2SnMe_3Cl + (Ph_2PC_2H_4PPh_2)_2Co(BPh_2)_2 \rightarrow 2Me_3SnBPh_2 + (Ph_2PC_2H_4PPh_2)_2CoCl_2$$

The corresponding bromine compounds $Me_nSn(BBr_2)_{4-n}$ are similarly prepared,[340] but can be isolated only as an adduct with excess of the tetraphenyldiphosphinoethane.

DERIVATIVES WITH LEAD SUBSTITUENTS

Plumbylboranes of type R_3PbBPh_2 and $R_2Pb(BPh_2)_2$ [$R=Me, Ph$] are orange or yellow and have been prepared by the interaction of compounds of type R_3PbX and R_2PbX_2 [$X=Cl, Br$] respectively with $(Ph_2PC_2H_4PPh_2)_2Co(BPh_2)_2$.[341] Reddish compounds of formula R_3PbBBr_2 and $R_2Pb(BBr_2)_2$ have been prepared analogously.[341] These compounds contain one or more covalent Pb—B bonds and, surprisingly, some of them are thermally rather more stable than the tin analogues. Though none of them can be stored indefinitely at room temperature, some need to be heated to 70°C to effect fairly rapid decomposition. This is true, for example, of the light-orange compound Me_3PbBPh_2, which melts with decomposition at 98–104°C. Infrared and ^{11}B n.m.r. spectra have been recorded.[341] Chemically, the compounds are very sensitive to oxygen, and the Pb—B bonds are ruptured by Br_2 or monovalent silver, which is reduced to the metal. The compounds form adducts with donors like tetraphenyldiphosphinoethane and enhance their stability by so doing.[341]

DERIVATIVES WITH NITROGEN SUBSTITUENTS

General

Attention will be confined here to those derivatives of borane(3) that contain one or more boron-nitrogen bonds. Those with only one such bond and of formula type H_2BNRR' ($R, R'=H$, alkyl, aryl, etc.) were formerly known as aminoboranes, but are now frequently termed boranamines. When there are two or three B—N bonds, however, it is generally more convenient to retain the terminology di- and triaminoborane respectively, so avoiding needlessly clumsy nomenclature. The total number of known nitrogen derivatives of BH_3 is exceedingly large, and only typical representatives will be included here.

Boranamines (Aminoboranes)

BORANAMINE

Monomeric boranamine (aminoborane) H_2BNH_2, the simplest nitrogen derivative of BH_3, was not definitely reported until 1970,[342] although evidence for its existence was found earlier.[343, 344] The preparation was a cryochemical one, depending on the quenching to $-196°C$ of pyrolyzing borazine vapour,[342] followed by the low-temperature high-vacuum fractionation of the products, from which H_2BNH_2 begins to distil at about $-160°C$. The monomer is stable at $-196°C$, but begins to polymerize at slightly higher temperatures: however, even at $-78°C$ polymerization is still moderately slow, but increases rapidly with temperature. Apart from the evidence provided by its volatility, the monomeric H_2BNH_2 was positively identified by infrared and mass spectrometry. Little else is known about its properties, except that its ionization potential is $11{\cdot}0 \pm 0{\cdot}1$ eV. It has however been the object of theoretical study. An *ab initio* treatment[345] yields a barrier to internal rotation about the B—N bond of 40·7 kcal mol^{-1} and a dipole moment of 2·071 D, but overall agreement with extended Hückel and CNDO calculations is not good. The derived bond polarity

$$\overset{+}{B}—\overset{-}{N}$$

is supported by another independent study,[346] notwithstanding a large implied contribution of π bonding. An *ab initio* estimation of the bond length is 1·378 Å, while that for the barrier to internal rotation about the B—N bond is here 33·3 kcal mol^{-1},[347] values which would be compatible with a strong B—N bond.

The longer known polymeric boranamine can be formed by the action of diborane(6) on ammonia,[348] lithium amide[349] or potassium aminotrimethylborate:[162]

$$NH_3 + \tfrac{1}{2}B_2H_6 \xrightarrow{100°C} \frac{1}{n}(BH_2NH_2)_n + H_2$$

$$LiNH_2 + B_2H_6 \xrightarrow[Et_2O]{-64°C} \frac{1}{n}(BH_2NH_2)_n + LiBH_4$$

$$K[H_2N.BMe_3] + 1\tfrac{1}{2}B_2H_6 \xrightarrow[Et_2O]{-78°C} \frac{1}{n}(BH_2NH_2)_n + KBH_4 + B_2H_3Me_3$$

The degree of polymerization is linked to the temperature of preparation. The high temperature needed for the first reaction (which is equivalent to pyrolyzing $H_3N.BH_3$) leads to a high value for n, whereas the product from the second reaction leads to short chains with a value of n between 3 and 5.[350] Both products are amorphous. In contrast, however, crystalline cyclic compounds with values of n between 2 and 5 may be prepared from $NaNH_2$ and $[BH_2(NH_3)_2][BH_4]$ in liquid ammonia,[343, 351] and are considerably more stable thermally and hydrolytically than the chain-like polymers. The dimer and trimer may be regarded as derivatives of B_2H_6 and B_3H_9 respectively. The dimer slowly converts to the trimer on standing in solution at room temperature.[343] The trimeric compound cyclotriboranamine or cyclotriborazane, $(BH_2NH_2)_3$, has also been prepared by reduction of a borazine salt:[352]

$$2B_3N_3H_6.3HCl + 6NaBH_4 \rightarrow 2(BH_2NH_2)_3 + 3B_2H_6 + 6NaCl$$

Particularly in the case of the amorphous products consisting of molecules with short chains, it is surprising that they do not cyclize to give the more stable cyclic isomers. No reason for the lack of such cyclization is immediately forthcoming. The properties of amorphous boranamines differ remarkably from those of the cyclic compounds. The latter, notwithstanding their severely restricted volatilities (associated with an appreciable polar character), will nevertheless sublime on heating in a vacuum: thus $(BH_2NH_2)_3$ sublimes at 100°C and only loses hydrogen slowly at 150°C.[352] The amorphous material, even when its average chain length is only 3·5, will not sublime, but commences to decompose if heated above 60°C.[350] And whereas the cyclic compounds are soluble in a variety of organic solvents, the amorphous preparations are insoluble in most, but dissolve in the strongly polar inorganic solvents dimethylsulphoxide and ammonia. In the infrared spectra the N—H stretching frequencies are well resolved with the cyclic species, but appear only as a broad unresolved band in the case of the amorphous species.[350] The kinetics of thermal decomposition of (presumably) amorphous boranamine have been studied over the range 70–120°C:[353] the energy of activation is reported as $28{\cdot}9 \pm 1{\cdot}2$ kcal mol^{-1} for the solid and $26{\cdot}7 \pm 0{\cdot}8$ kcal mol^{-1} for the 'melt'. It however needs to be emphasized that none of the other investigators report that $(BH_2NH_2)_x$ can be melted, but speak of a thermal decomposition to other not clearly specified boron-nitrogen compounds. It has been shown that on heating to 205°C for 2·5 h the cyclic trimer $(BH_2NH_2)_3$ breaks down to borazine $B_3N_3H_6$.[352] Moreover, the amorphous variety reacts at or below room temperature with H_2O, MeOH, NH_3 and NMe_3, being converted by excess of the latter to $H_3B.NMe_3$ plus a non-volatile amorphous white solid,[350] whereas the cyclic compounds are not attacked under the same conditions.

N-ALKYLBORANAMINES

The effect of progressive alkylation at the nitrogen atom is interesting. Thus N-methylboranamine or (methylamino)borane, BH_2NHMe, is known only as a cyclic trimer (two isomers) and a linear polymer. The trimer 1,3,5-trimethylcyclotriboranamine, is prepared by the controlled pyrolysis of O,N-dimethylhydroxylamine borane or, better, of methylamine borane[354]

$$3H_3B.NH_2Me \xrightarrow{100°C} (BH_2NHMe)_3 + 3H_2$$

Other methods of preparing it include the reaction of sodium tetrahydroborate with the hydrochloride of methylamine[355] or of 1,3,5-trimethylborazine[355] and the reaction of diborane(6) with lithium methylamide:[356]

$$3NH_3MeCl + 3NaBH_4 \xrightarrow[\text{monoglyme}]{85°C} 3NaCl + (BH_2NHMe)_3 + 6H_2$$

$$2B_3H_3N_3Me_3.3HCl + 6NaBH_4 \xrightarrow[\text{monoglyme}]{25°C} 6NaCl + 2(BH_2NHMe)_3 + 3B_2H_6$$

$$3LiNHMe + 4B_2H_6 \xrightarrow[Et_2O]{0°C} 3LiBH_4 + \tfrac{1}{3}(BH_2NHMe)_3 + 2\mu\text{-}B_2H_5NHMe$$

(With the last reaction, the temperature must be kept close to 0°C, as a competing reaction predominates at room temperature.) The isolated product is relatively stable well above 100°C, though stronger heating (180–200°C) breaks it down into 1,3,5-trimethylborazine.[354, 357] It is only very slowly hydrolyzed by cold water. Physical investigations have revealed the presence of two isomers, which can be separated by fractional sublimation *in vacuo* or fractional crystallization from C_6H_6 or MeOH.[355] In liquid ammonia solution at room temperature, however, the isomers undergo interconversion at a measurable rate with a free-energy change of $0{\cdot}51 \pm 0{\cdot}3$ kcal mol^{-1}. Single-crystal X-ray studies have established the chair configuration for both isomers; the more stable, less volatile and less soluble isomer I with all 3 methyl groups in equatorial positions, isomer II with 2 groups equatorial and 1 axial. Certain chemical differences exist: for example, isomer I forms a 2,4,6-trichloro derivative with HCl at 0°C, isomer II only a 2,4-dichloro derivative.[358]

The polymeric form $(BH_2NHMe)_x$ is a non-volatile colourless solid formed in the gas-phase transamination of BH_2NMe_2 by methylamine:[359]

$$BH_2NMe_2 + NH_2Me \xrightarrow[\text{vapour phrase}]{60°C} \frac{1}{x}(BH_2NHMe)_x + NHMe_2$$

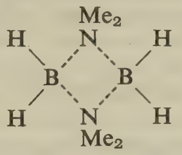
This form of N-methylboranamine has a distinctive infrared absorption spectrum and is insoluble in solvents used for dissolving the trimer. Although thermodynamically less stable, it is not converted to the trimer on heating, but decomposes with the loss of H_2 above 160°C. However, it is partly convertible to the trimer by the catalytic action of a trace of dimethylamine over several hours at 55–75°C.[359]

N,N-DIALKYLBORANAMINES

The usual form of N,N-dimethylboranamine, at least in the liquid and vapour phases, is an equilibrium mixture of the monomer and dimer:

$$2BH_2NMe_2 \rightleftharpoons (BH_2NMe_2)_2$$

This is in contrast to the monomethyl compound. A stable trimer and an unstable amorphous polymer are also known. At room temperature, N,N-dimethylboranamine exists essentially as the crystalline dimer, $\mu\mu$-bis(dimethylamino)diborane (pp. 93–94)



which is volatile. Study of the vapour has further shown that the above equilibrium is accompanied by the reversible disproportionation reaction[360]

$$3BH_2NMe_2 \rightleftharpoons BH(NMe_2)_2 + \mu\text{-}B_2H_5NMe_3$$

Thus the enthalpy change for the dissociation of 1 mole of dimer to 2 moles of monomer as originally calculated from dissociation-pressure data, *c.* 20 kcal mol^{-1},[348] has since been corrected to allow for the accompanying disproportionation and a new free-energy equation derived, from which $\Delta G°_{298\cdot16} = 5\cdot56$ kcal mol^{-1}.[360] The enthalpies of dissociation in the liquid phase have been determined for a number of analogues by means of n.m.r. techniques.[361]

Monomeric BH_2NMe_2 is formed directly at the reaction temperature when diborane(6) is heated with dimethylamine[348, 362]

$$B_2H_6 + 2NHMe_2 \xrightarrow{130\text{–}200°C} 2BH_2NMe_2 + 2H_2$$

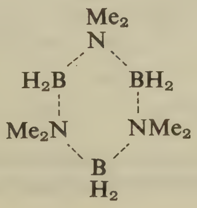
Apart from methods analogous to those cited for preparing BH_2NHMe, other methods for preparing the N,N-dialkylboranamines are known, such as the removal of BH_3 from $R_2NB_2H_5$ by certain Lewis bases,[363] the thermal decomposition of the bis-borane adduct of the corresponding tetraalkylhydrazine at 100°C,[364]

$$R_4N_2.2BH_3 \xrightarrow{100°C} 2BH_2NR_2 + H_2$$

the reduction of the corresponding B-chloroborane with tributylstannane,[365] and the simple fission of hydrogen at 180–200°C from the dialkylamine borane:[348]

$$R_2NH.BH_3 \xrightarrow{190°C} BH_2NR_2 + H_2$$

The degree of dimerization is not precisely predictable, but varies with the nature of the radical R. Nor can it be assumed that it is always the dimer that is formed in the case of analogues. The trimer, $(BH_2NMe_2)_3$, does not take part in any of the aforementioned equilibria. It is formed irreversibly by heating the dimer with B_5H_9 (or other higher borane),[366] the amount of B_5H_9 destroyed being strictly proportional to the amount of trimer formed.[367] It has a camphor-like odour, melts at 97·0–97·8°C, and is stable at temperatures up to 300°C. Its cyclic structure has been well established by X-ray diffraction studies.[368, 369]



The ring is non-planar and chair-shaped. The hydridic character of the H atoms on the boron atoms is so markedly reduced that the compound does not hydrolyze in the cold and is quite unreactive towards moist air.[366] In addition to these forms, an amorphous polymer which does not melt is known, but it is formed with difficulty by heating the dimer at high pressures (3000 atm) and readily depolymerizes to the dimer, even at room temperature.[370, 371]

The physical properties of some N,N-dialkylboranamines and related compounds have been recorded.[372] The photoelectron spectra and ionization energies of BH_2NMe_2 and several related compounds have been studied.[373] Evidence indicates that the ionization process involves a π electron, and ultraviolet spectra are interpreted in terms of $\pi \rightarrow \pi^*$ transitions.[374] The kinetics of thermal decomposition of the diethyl analogue, BH_2NEt_2, are first order with an energy of activation of $27{\cdot}4 \pm 0{\cdot}7$ kcal mol^{-1}.[375] In these compounds, the bonding of a nitrogen atom to the boron atom does not totally remove the acceptor properties of the latter. Thus, the adducts $Me_3N.BH_2NMe_2$[360] and $C_5H_5N.BH_2NMe_2$[376] are both known. The products of reacting BH_2NMe_2 with LiH,[377] B_2H_6,[356] and HCl[348] or PCl_5[378] are $Li[H_3BNMe_2]$, μ-$B_2H_5NMe_2$ and $B(NMe_2)Cl_2$ respectively.

Diaminoboranes

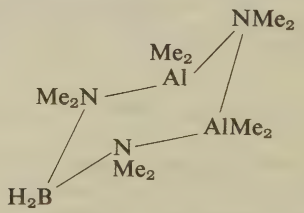
Although a number of doubly nitrogen-substituted boranes are known, the parent member of the series, diaminoborane $BH(NH_2)_2$, has not been isolated. However, bis(dimethylamino)borane $BH(NMe_2)_2$ is well established and was first prepared by prolonged heating of BH_2NMe_2 with excess dimethylamine:[379]

$$BH_2NMe_2 + NHMe_2 \xrightarrow[10\ h]{200°C} BH(NMe_2)_2 + H_2$$

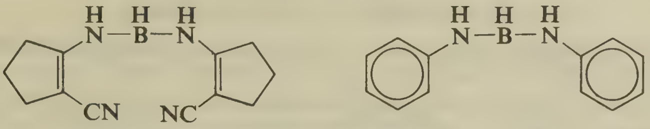
It is also formed in the reversible disproportionation of BH_2NMe_2,[360] and a study has been made of the conversion of the latter by the action of Lewis bases to $BH(NMe_2)_2$ and $B(NMe_2)_3$.[363] Other methods of preparing $BH(NMe_2)_2$ include the reduction of $B(NMe_2)_2Cl$ with $LiAlH_4$[380] or LiH[381] and the pyrolysis of the borane(3) adduct of tetramethylhydrazine:[364]

$$N_2Me_4.BH_3 \xrightarrow{100°C} BH(NMe_2)_2 + H_2$$

Unlike BH_2NMe_2, $BH(NMe_2)_2$ exhibits no tendency to polymerize, but has the characteristics of a strictly monomeric volatile liquid of f.p. −45°C and b.p. (extrapolated) 109°C.[379] Its ultraviolet,[374] photoelectron[373] and ^{11}B n.m.r. spectra[382] have been investigated, as has the ^{14}N n.m.r. spectrum of the closely related compound $BH(NEt_2)_2$.[383] Chemical as well as physical properties are affected by the increased substitution at the boron atom. Thus the acidic properties are decreased in accordance with expectation, so that the bis-substituted borane no longer forms a trimethylamine adduct that is sufficiently stable to be isolated.[360] On treatment with B_2H_6, $BH(NMe_2)_2$ is converted to BH_2NMe_2,[360] while with trimethylaluminium the cyclic compound 1,1,2,2,3,3,4,4,5,5-decamethyl-6,6-dihydro-1,3,5-triaza-2,4-dialumina-6-boracyclohexane[384]



is formed. With HCl, $BH(NMe_2)_2$ gives the bis adduct $BH(NMe_2)_2.2HCl$ or $[BHCl(NMe_2)_2]^+Cl^-$:[381] other bis(dialkylamino)boranes react differently and undergo B—N bond cleavage, however. The related compounds bis(2-cyano-1-cyclopentenylamino)-borane and bis(2-cyanophenylamino)borane



have been formed by treating the appropriate amine with diborane(6), but in the latter case other products result if the temperature is not kept close to 20°C.[385]

Triaminoboranes

TRIAMINOBORANE (BORON AMIDE)

The simplest triply nitrogen-substituted borane(3) is triaminoborane $B(NH_2)_3$, also named boron amide. This has long been known from the reaction of boron trichloride with ammonia:

$$BCl_3 + 6NH_3 \rightarrow B(NH_2)_3 + 3NH_4Cl$$

but the product has variable composition unless the temperature of reaction is kept low and carefully controlled:[386] it has not so far been well characterized. Triaminoborane appears to be stable at 0°C and possibly some way above, but on heating loses ammonia slowly to give boron imide $B_2(NH)_3$, and at really high temperatures boron nitride. It has thus been proposed as a source of highly pure BN.[387] The amount of π bonding in $B(NH_2)_3$ and many related compounds has been predicted from LCAO-MO studies.[388]

TRIS(ORGANOAMINO)BORANES

The simpler members of the analogous series of tris(alkylamino)- and especially tris(dialkylamino)boranes, $B(NHR)_3$ and $B(NR_2)_3$, have been much better characterized as volatile liquids or solids that are soluble in most organic solvents, hydrolyze readily, and hence smell of the parent amine. The former series is prepared from boron trichloride and the corresponding primary amines:[389, 390]

$$BCl_3 + 6RNH_2 \xrightarrow{-78°C} B(NHR)_3 + 3NH_3RCl$$

If boron trifluoride is used instead of the trichloride, the presence of an alkali metal[391] or a Grignard reagent[392] is required:

$$BF_3 + 3EtNH_2 + 3Li \rightarrow B(NHEt)_3 + 3LiF + 1\tfrac{1}{2}H_2$$

In some cases it is convenient to make use of a transamination reaction, in which a less volatile amine displaces a more volatile one on heating.[393, 394] It may also be formed by the thermal decomposition of the borane(3) adduct of the base in the presence of excess base:[395]

$$H_3B.NH_2R + 2NH_2R \rightarrow B(NHR)_3 + 3H_2$$

The use of a secondary amine R_2NH instead of a primary in these methods leads quite generally to the formation of the tris(dialkylamino)boranes, $B(NR_2)_3$ and $B(NRR')_3$, though with sterically hindered diamines such as $NH(i\text{-}Pr)_2$ or $NHPh_2$ the reaction with BCl_3 stops at the $B(NR_2)_2Cl$ stage.[396] Preparations from borate esters,[397] thioborate esters[398] and boron sulphide[398] are also possible, but the reaction of boron trifluoride etherate with the N-lithio derivative of the amine in refluxing tetrahydrofuran-hexane solvent is especially recommended for its high yield and low sensitivity to steric effects[399]

$$3LiNRR' + BF_3.OEt_2 \xrightarrow[\text{THF-hexane}]{\text{reflux, 3 h}} B(NRR')_3 + 3LiF + Et_2O \qquad [R, R' = \text{alkyl, aryl}]$$

The N-lithio reactant is readily prepared from the amine and *n*-butyllithium in the same solvent at 0°C. The N-alumino compound, $LiAl(NMe_2)_4$, prepared from $LiAlH_4$ and

$NHMe_2$, can be used similarly.[400] Provided the N-lithio reactant is kept in excess, it will also react with diborane(6) to give the required triaminoborane:[356, 401]

$$3LiNR_2 + 2B_2H_6 \rightarrow B(NR_2)_3 + 3LiBH_4$$

This reaction is therefore unlike that of $LiNH_2$, which gives polymeric boranamine $(H_2BNH_2)_x$ (p. 93).

Tris(alkylamino)- and tris(dialkylamino)boranes have been much studied with respect to their physical properties, including their infrared,[402, 403] Raman,[403] ultraviolet,[374] photoelectron[373] and ^{11}B and ^{14}N n.m.r. spectra,[382, 383, 404, 405] as well as for their bond contributions to the molecular refractions,[406] magneto-optical rotations[407] and diamagnetic susceptibilities.[408] The evidence points to an appreciable contribution from π bonding to the B—N bond. The enthalpy of formation of liquid $B(NMe_2)_3$ is $-77{\cdot}1 \pm 1{\cdot}0$ kcal mol^{-1},[409] which (in conjunction with a more recent value for the enthalpy of atomization of boron) corresponds to a mean dissociation energy of 102·1 kcal mol^{-1} for the B—N bond, a value sensibly higher than that for the C—C bond in neopentane. The stretching force constant of the B—N bond, *c.* $5{\cdot}5 \times 10^5$ dyne cm^{-1},[403] also indicates a strengthening above simple σ bonding, as does the comparatively short bond length of 1·431 Å established by electron-diffraction measurement in the gas phase.[410] The experimental data, although compatible with a planar BN_3 skeleton, indicate that the angle through which, for steric reasons, the —NMe_2 groups are twisted with respect to the BN_3 plane is 32·8°, notwithstanding the degree of boron-nitrogen π bonding. The concept of partial double-bond character of the B—N bonds finds support in the results of n.m.r. studies on N,N-disubstituted boranamines, which indicate activation energies of internal rotation about the B—N bonds as high as 50–100 kJ mol^{-1}.[411, 412]

The difference in thermal stability between compounds of types $B(NHR)_3$ and $B(NR_2)_3$ is considerable. The former decompose to substituted borazines[389, 413]

$$3B(NHEt)_3 \xrightarrow{200°C} (EtNHBNEt)_3 + 3NH_2Et$$

whereas the latter cannot decompose in this way and are stable to much higher temperatures, e.g. $B(NMe_2)_3$ and $B(NMePh)_3$ will withstand 280°C for 48 h.[414] When the ligands are not identical, they also exhibit considerable resistance to disproportionation, but nevertheless enter into redistribution reactions with trialkylboranes[415] or boron halides:[416–18]

$$B(NR'_2)_3 + 2BR_3 \rightarrow 3R_2BNR'_2 \qquad [R = \text{alkyl, Cl, Br; } R' = \text{alkyl}]$$

Attempts to effect a similar reaction with a trialkylborate failed.[416] Tris(dialkylamino)boranes show no tendency to form addition compounds with donors such as pyridine.[396] If a donor reacts at all, rupture of the B—N bond occurs. Thus hydrolysis to boric acid is effected quite rapidly by water or an acetone-water mixture,[419] and still more rapidly by acids:[409]

$$B(NMe_2)_3 + 3H_2O + 3HCl \xrightarrow{H_2O} B(OH)_3 + 3NH_2Me_2Cl$$

With alcohols, e.g., butanol, a stepwise alcoholysis occurs:[416]

$$B(NEt_2)_3 + BuOH \xrightarrow{-20°C} BuOB(NEt_2)_2 + NHEt_2$$

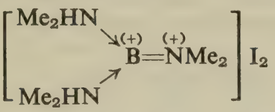
the ultimate product being the trialkylborate $B(OBu)_3$. The B—N bonds of $B(NMe_2)_3$ are cleaved by many oxygen-containing compounds, including acetic acid, ketones, phenol and compounds containing the $\rangle$NOH group,[420] the result being displacement of the dialkylamine. A similar displacement reaction with thiols is apparently only partial, at least when occurring between $B(NEt_2)_3 + n$-BuSH.[421] Under anhydrous conditions, $B(NMe_2)_3$ does not form a stable boronium salt of type $[BH(NMe_2)_3]Cl$ with HCl, but undergoes cleavage of one of the B—N bonds:[418]

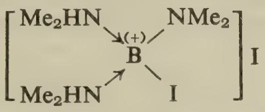
$$B(NMe_2)_3 + 2HCl \xrightarrow{c.\,-10°C} B(NMe_2)_2Cl + NH_2Me_2Cl$$

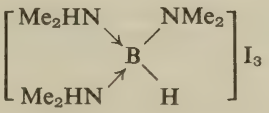
Excess of HCl however leads to the formation of $[Cl_2B(NHMe_2)_2]Cl$. The reaction of $B(NEt_2)_3$ is different, all three B—N bonds being cleaved:[418]

$$B(NEt_2)_3 + 5HCl \xrightarrow{c. -10°C} Cl_3B.NHEt_2 + 2NH_2Et_2Cl$$

With HI, tris(dimethylamino)borane gives the bis adduct $B(NMe_2)_3.2HI$,[422] which, although it has been assigned the formulation (I) purely on the strength of an observed infrared frequency at 1558 cm^{-1}, might for energetic reasons be expected to have the structure (II). A tris adduct, $B(NMe_2)_3.3HI$, is formed more slowly: the structure is uncertain, but could be


(I)


(II)



Many other substances are capable of liberating dimethylamine from $B(NMe_2)_3$, including carboxylic acids and their anhydrides, ketones, phenols and compounds containing the NOH group.[420] Boron-oxygen bonds are normally formed. The $—NMe_2$ ligands can be exchanged not only with other amino groups in typical transamination reactions, but with other nitrogen-containing groups such as the diphenylketimino group,[423] with alkoxy groups (e.g. of a sulphenic ester)[424] and with chlorine:[425, 426]

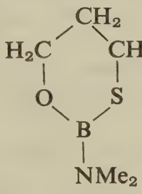
$$B(NMe_2)_3 + nPh_2C{:}NH \rightarrow (Ph_2C{:}N)_nB(NMe_2)_{3-n} + nNHMe_2$$

$$B(NR_2)_3 + 3PhSOMe \rightarrow B(OMe)_3 + 3R_2NSPh$$

$$B(NMe_2)_3 + TiCl_4 \rightarrow B(NMe_2)_{3-x}Cl_x + Ti(NMe_2)_xCl_{4-x} \qquad [x = 1, 2]$$

$$B(NMe_2)_3 + COCl_2 \rightarrow B(NMe_2)_2Cl + Me_2NC(O)Cl$$

With 3-mercaptopropanol, $B(NMe_2)_3$ gives with displacement of two molecules of amine the B-heterocyclic compound:[427]



Among the less predictable reactions of $B(NMe_2)_3$ is the formation of a tricarbonyltungsten complex and analogous complexes containing other metals[428]

$$B(NMe_2)_3 + (MeCN)_3W(CO)_3 \rightarrow (Me_2N)_3B.W(CO)_3 + 3MeCN$$

In these the substituted triaminoborane is apparently assuming the role of a π-donor ligand.

An interesting insertion reaction occurs with carbon dioxide:[429]

$$B(NMe_2)_3 + 3CO_2 \xrightarrow[24\ h]{20°C} B(OC(O)NMe_2)_3 \qquad (\text{yield} > 60\%)$$

A similar reaction occurs with carbonyl sulphide, except that only two of the three B—N bonds yield to the insertion[426]

$$B(NMe_2)_3 + 2COS \xrightarrow[36\ h]{20°C} Me_2NB(OC(S)NMe_2)_2$$

No reaction occurs with carbon disulphide.[429]

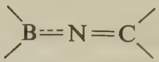
Many arylaminoboranes such as tris(anilino)borane $B(NHPh)_3$, m.p. 166–169°C,[430] and tris(diphenylamino)borane $B(NPh_2)_3$, m.p. 247–248°C,[394] have been prepared. They often possess a relatively high stability.

Other Nitrogen-substituted Boranes

Known compounds not falling into the above categories include tripyrrolylborane $B(NC_4H_4)_5$, m.p. 211–212°C, preparable in a number of ways from pyrrolylpotassium, e.g.

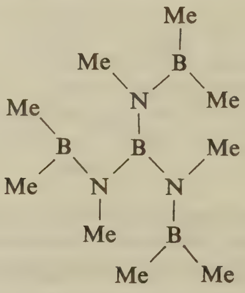
$$BCl_3 + 3K(NC_4H_4) \rightarrow B(NC_4H_4)_3 + 3KCl$$

and giving the salt $K[B(NC_4H_4)_4]$ with excess.[431] In other cases the nitrogen may be involved in double bonding within the ligands, as in the substituted methyleneaminoboranes $B(N{=}CPh_2)_3$,[432, 433] and $B(N{=}C(CF_3)_2)_3$.[434, 435] Compounds of this type have been the subject of a recent review.[436] They are frequently termed 'iminoboranes'—a misnomer, since they do not contain the —B═NH grouping (see p. 436). In the monomeric examples the B—N bond order is greater than unity, so that these compounds present a reactive allene-like system with cumulative multiple bonds:



The same may be true of tris(isothiocyanato)borane $B(N{=}C{=}S)_3$, which exists both as a liquid boiling at 92°C under 0·1 Torr pressure, and also as a solid.[437] The boron is nevertheless not coordinatively saturated, since the compound shows Lewis-acid characteristics and forms adducts with tertiary amines, pyridine and nitriles.[437] Tris(isocyanato)borane $B(NCO)_3$ shows no volatility and is presumably not monomeric.[438, 439] Bis(3,5-dimethylpyrazolyl)borane $BH(N_2C_3HMe_2)_2$ is worth mentioning, since it exists as a dimer without the usual hydrogen-bridge bonding. Instead the dimer is held together by two equivalent dative bonds, one from the second nitrogen atom of one of the two pyrazolyl groups of each half of the molecule to the boron atom of the other half.[440]

Study has been extended to substituted aminoboranes in which the nitrogen is linked to non-metals other than carbon. Thus, by using BMe_2Br for substitution purposes, the very interesting substance tris-(N-(dimethylboryl)methylamino)borane[441]



(and other related compounds) may be prepared from the appropriate (trimethylsilylamino)borane (*v.i.*). It is a colourless viscous liquid which can be distilled in vacuum and which oxidizes in the air only slowly. The ^{11}B and ^{14}N n.m.r. spectra have been reported.[441] Related to this compound are the silylaminoboranes. The first to be reported was $BH_2N(SiH_3)_2$, which exists in three forms, namely a monomer with a vapour pressure of 7 Torr at −78°C, a metastable dimer (v.p. 10 Torr at 25°C), and a nonvolatile polymer formed irreversibly on heating either of the other forms.[442] It is prepared from bromodiborane(6) and trisilylamine:

$$2B_2H_5Br + 2N(SiH_3)_3 \xrightarrow[18\ h]{-78^{\circ}C} 2BH_2N(SiH_3)_2 + 2SiH_3Br + B_2H_6$$

Refs. p. 439

Tris-(N-(trimethylsilyl)methylamino)borane (b.p. 55–57°C at 0·001 Torr) has likewise been prepared from boron tribromide:[443]

$$BBr_3 + 3NMe(SiMe_3)_2 \rightarrow B(NMeSiMe_3)_3 + 3SiMe_3Br$$

These preparations and that of the (dimethylboryl)amino compound mentioned above illustrate the ready cleavage of the Si—N bond by bromoboranes. Germylamino- and stannylaminoboranes are known to date only with mixed ligands (p. 422).

Examples of substituted boranes containing the N—N link include hydrazinoboranes. The high-temperature pyrolysis of hydrazine borane $H_3B.N_2H_4$ leads to the polymeric bis-1,2-borylhydrazine $(H_2BNHNHBH_2)_n$.[444] But in liquid hydrazine the elimination of hydrogen to give N-aminoboranamine, the simplest hydrazinoborane, proceeds catalytically and has been the subject of rate studies at 50–100°C[445]

$$H_3B.N_2H_4 \rightarrow H_2BNHNH_2 + H_2$$

In general, hydrazinoboranes are readily prepared by transamination reactions, as is, for example, tris-(2,2-dimethylhydrazino)borane $B(NHNMe_2)_3$ (m.p. 102–103°C):[446]

$$B(NMe_2)_3 + 3H_2NNMe_2 \rightarrow B(NHNMe_2)_3 + 3NHMe_2$$

In a study of the crystal and molecular structure, the B—N bond length has been observed to be 1·420 Å, which is short for a triaminoborane.[447] The bond is still sufficiently reactive, however, to undergo an insertion reaction with carbon dioxide:[426]

$$B(NHNMe_2)_3 + 3CO_2 \rightarrow B(OCONHNMe_2)_3$$

The azidoboranes $BH_2(N_3)$, $BH(N_3)_2$ and $B(N_3)_3$ are formed from the controlled interaction of diborane(6) with hydrogen azide in ether solution[448]

$$B_2H_6 + 6HN_3 \xrightarrow[-20\,^{\circ}C]{Et_2O} 2B(N_3)_3 + 6H_2$$

These and related compounds have been reviewed in detail.[449] Azidoborane $BH_2(N_3)$, also formed from B_2H_6 and NaN_3, is not monomeric, the degree of association depending on the concentration: cryoscopic measurements in benzene extrapolated to infinite dilution correspond to a molecular weight intermediate between the values for the dimer and trimer.[450] The triazide $B(N_3)_3$ is an explosive crystalline substance soluble in ether (though even the heat of solution may cause the solid to detonate!) and is volatile in a high vacuum.[448] It also detonates in contact with water vapour, but at low temperatures it adds on HN_3 reversibly to form the unstable complex tetraazidoboric acid, $HB(N_3)_4$, which is a liquid at -60°C. Alternatively it will react additively with sodium azide to give the more stable sodium salt $NaB(N_3)_4$.

A borane with sulphur-substituted amino ligands is tris(trifluoromethylmercaptoamino)borane $B(NHSCF_3)_3$ from the reaction[451]

$$BCl_3 + 3CF_3SNH_2 \rightarrow B(NHSCF_3)_3 + 3HCl$$

Sulphur-substituted imidino ligands occur in tris(dimethyloxosulphuranylideneamino)borane $B(—N{=}S(O)Me_2)_3$ (m.p. 176–178°C), which is readily prepared from S,S-dimethyl-N-(trimethylsilyl)sulphoximide and boron trifluoride etherate:[452]

$$BF_3.OEt_2 + 3Me_2S(O)NSiMe_3 \xrightarrow[MeCN]{} B(NS(O)Me_2)_3 + 3SiMe_3F + Et_2O$$

Saturated B-Organoboranamines

Nitrogen-substituted boranes with mixed ligands include B-substituted boranamines of types R_2BNH_2, R_2BNHR' and $R_2BNR'_2$, which are commonly mixtures of monomers and dimers; and also compounds of types $RB(NHR')_2$ and $RB(NR'_2)_2$, which are normally monomeric. No compound of type $RB(NH_2)_2$ has been reported. Otherwise all the said types are well represented in the literature, although only the simpler examples will receive mention here.

The methyl compounds Me_2BNH_2, Me_2BNHMe and Me_2BNMe_2 exhibit exceptionally interesting properties and were originally prepared by heating the adduct of trimethylborane and ammonia or the appropriate amine in a sealed tube at a controlled temperature:[357, 453–6]

$$Me_3B.NH_3 \xrightarrow[2\ h]{280^\circ C,\ 20\ atm} CH_4 + Me_2BNH_2$$

$$Me_3B.NH_2Me \xrightarrow[several\ hours]{310\ C,\ 26\ atm} CH_4 + Me_2BNHMe$$

$$Me_3B.NHMe_2 \xrightarrow{330^\circ C,\ pressure} CH_4 + Me_2BNMe_2$$

(If the temperature and pressure are allowed to rise appreciably higher, Me_2BNH_2 and Me_2BNHMe begin to lose more methane and are converted into the borazines $(MeBNH)_3$ and $(MeBNMe)_3$ respectively: Me_2BNMe_2 is however thermally more stable, since it cannot decompose in this way.) The sealed tube can probably be dispensed with, since it has more recently been discovered that preparations of this type occur at much lower temperatures in the presence of a dialkylboryl pivalate.[457]

In the vapour phase these compounds are essentially monomeric, and rapid cooling of the vapour originally produces a very volatile monomeric liquid with its own characteristic vapour pressure. However, the monomeric form proceeds gradually to establish equilibrium with the dimeric (or other polymeric) form, a process that is accompanied by a drop in the vapour pressure. Two vapour-pressure equations may thus be derived, one for the monomer, and one for the equilibrium mixture. Establishment of equilibrium is rather slow, depending on the temperature, so that a true equilibrium vapour pressure is not immediately established, and the observed vapour-pressure curve may manifest considerable hysteresis effects on reversing the direction of temperature change. Suddenly frozen monomeric Me_2BNH_2 vapour melts only a little above the temperature of liquid nitrogen, has a vapour pressure of 25 Torr at −64·2°C and an extrapolated boiling point of 4°C.[357] Above room temperature the degree of dimerization in the vapour is almost negligible, but at −19°C amounts to about 12 %. For the equilibrated liquid state at 9°C, on the other hand, the equilibrium lies largely in favour of the dimer

$$2Me_2BNH_2 \rightleftharpoons B_2Me_4(NH_2)_2$$

while for the solid that slowly crystallizes out below its m.p. of 9°C, dimerization is complete. The enthalpy of dimerization, calculated from the equilibrium constant for the vapour over the temperature range −19°C to +6·4°C, amounts to −10 kcal per 2 moles of monomer in fair agreement with the value −10·7 obtained from n.m.r. studies.[361] The infrared[458–60] and Raman[460, 461] spectra of Me_2BNH_2 and isotopic species, as well as of related compounds, have been reported and discussed. Chemically the monomeric form of Me_2BNH_2 is much more reactive than the dimeric. The dimer does not react with hydrogen chloride unless it first dissociates to the monomer, which reacts vigorously at room temperature with one molecule, and on heating with a second:[357]

$$Me_2BNH_2 \xrightarrow[20^\circ C]{HCl} Me_2ClB.NH_3 \xrightarrow[80^\circ C]{HCl} BMe_2Cl + NH_4Cl$$

It does not react with BMe_3 or BMe_2F, but undergoes a lively reaction with BF_3:[462]

$$Me_2BNH_2 + BF_3 \rightarrow Me_2BF + F_2BNH_2$$

At 330°C it pyrolyses to B,B′,B″-trimethylborazine.[357] Further chemical study of the compound is needed.

The very similar compound Me_2BNHMe is likewise monomeric in the gas phase and can be suddenly chilled to a monomeric liquid with a vapour pressure of 19 Torr at −45°C and an extrapolated b.p. of 38·3°C.[453] This slowly equilibrates with the dimeric form, but the equilibrium mixture is richer in monomer at room temperature and in dimer at low temperatures. A solid dimer is readily obtained in crystalline form on vaporizing the monomer under *vacuo*. The ^{11}B and ^{14}N n.m.r. spectra[383] have been reported, as well as the infrared[459] and Raman[461] spectra. Chemically Me_2BNHMe resembles Me_2BNH_2, but it has been little studied. It pyrolyses at 450°C to hexamethylborazine.[453]

The fully methylated analogue Me_2BNMe_2 is a mobile volatile liquid with a characteristic smell.[454, 456] In the gas phase it is monomeric, but it also undergoes dimerization (or possibly polymerization) in the liquid phase, which on freezing sets to a glass that exhibits no sharp melting point. Its infrared,[459, 460] Raman,[460, 461] n.m.r.,[383, 405] ultraviolet[40, 374] and photoelectron spectra[39, 373] have been recorded. The molecule has a near-planar skeleton with a B—N bond length of 1·42 Å.[463] Chemically, aside from its mode of pyrolysis, it resembles Me_2BNH_2 and Me_2BNHMe, for example, in its reaction with HCl.[454] It readily forms adducts. When it adds on to diboron tetrachloride at −78°C, it forms predominantly the 1:2 complex $B_2Cl_4.2Me_2NBMe_2$, which decomposes on warming to room temperature; but there is also evidence for the formation of an unstable 1:1 complex, $B_2Cl_4.Me_2NBMe_2$, through π donation from the $B\overset{\leftarrow}{-}N$ bond to the B—B bond.[464] A further example of a probable π complex of Me_2BNMe_2 is connected with its ability to displace one allyl group from bis(π-allyl)-nickel $Ni(\pi\text{-}C_3H_5)_2$ to give an orange-red oil of formula[465]

$$(\pi\text{-}C_3H_5)Ni(Me_2BNMe_2)_2$$

Evidence for π bonding between the BN system and the metal atom is provided by the infrared and ^{11}B n.m.r. spectra. In this compound it is possible to regard the incoming ligand as in the dimerized form and containing a four-membered $(BN)_2$ ring, though this is by no means certain. In solution the complex does not exhibit the paramagnetism expected for Ni(I), and so is presumably itself dimerized. That the B—N bond in Me_2BNMe_2 has partial double-bond character is supported by the almost planar C_2BNC_2 skeleton in the crystalline state,[463] which strongly implies internal π bonding —since otherwise the configuration around the nitrogen atom would be far from planar. Further, the barrier to internal rotation about the B—N bond for the closely related compound $Me_2BNMePh$ is determined by n.m.r. spectroscopy to be $10{\cdot}8 \pm 0{\cdot}7$ kcal mol^{-1},[412] and for other substituted boranamines may amount to more than twice this figure.[411] With mixed substituted boranamines such as PhBzBNMeBz the degree of π bonding is sufficient to enable *cis* and *trans* isomers to be isolated, and such isomers are not easily interconverted, although isomerization can be accomplished through irradiation with ultraviolet light.[466] Steric overcrowding about the nitrogen atom, as in Me_2BNPh_2, is accommodated by molecular distortions other than B—N bond rotation.[467]

Although there are no reported attempts to prepare $MeB(NH_2)_2$ and analogous B-substituted diaminoboranes such as $PhB(NH_2)_2$, there is no reason to expect that these should be incapable of existence. B,N-Dimethyl-B-methylaminoboranamine $MeB(NHMe)_2$ is readily prepared as a liquid boiling at 52°C under a pressure of 20 Torr from $MeBBr_2$ and methylamine in a non-aqueous solvent at low temperatures:[468]

$$MeBBr_2 + 4NH_2Me \xrightarrow[-60°C]{C_5H_{12},\ Et_2O} MeB(NHMe)_2 + 2NH_3MeBr$$

The n.m.r. spectra of this and related compounds have been studied.[72, 382, 383]

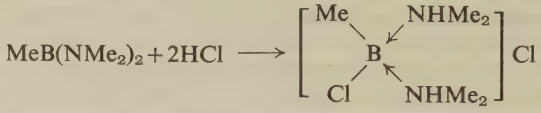
The first reported attempt to prepare $MeB(NMe_2)_2$ (from $ClB(NMe_2)_2$ and $ZnMe_2$[380]) led only to its disproportionation products, but this merely showed it to be thermodynamically unstable with respect to Me_2BNMe_2 and $B(NMe_2)_3$, into which it may be converted catalytically. B,N,N-Trialkyl-B-bis(alkylamino)boranamines $RB(NR_2)_2$ are in fact readily obtained in other ways, e.g.[13, 422]

$$RBCl_2 + 4NHMe_2 \xrightarrow[<0°C]{Et_2O} RB(NMe_2)_2 + 2NH_2Me_2Cl$$

$$ClB(NMe_2)_2 + LiR \xrightarrow[-78°C]{Et_2O} RB(NMe_2)_2 + LiCl$$

$$ClB(NMe_2)_2 + RMgBr \xrightarrow[20°C]{Et_2O} RB(NMe_2)_2 + \tfrac{1}{2}MgCl_2 + \tfrac{1}{2}MgBr_2$$

The simplest member of the series, $MeB(NMe_2)_2$, is a volatile liquid boiling at 29–32°C under a pressure of 15 Torr.[422] Its n.m.r.,[383, 405] ultraviolet[374] and photoelectron[373] spectra have been studied. Chemically it is sufficiently stable to be distilled under normal pressure without disproportionation, and shows so little sensitivity towards oxidation and moisture that it can be handled without difficulty in air.[422] It reacts with two molecules of HCl without bond rupture according to the equation



$$\mathrm{MeB(NMe_2)_2 + 2HCl \longrightarrow \left[\begin{array}{ccc} Me & & NHMe_2 \\ & B & \\ Cl & & NHMe_2 \end{array}\right]Cl}$$

whereas the propyl or butyl analogues react with two or three molecules of HCl with successive rupture of the B—N bonds:

$$\mathrm{RB(NMe_2)_2 + 2HCl \rightarrow RB(Cl)NMe_2 + NH_2Me_2Cl}$$

$$\mathrm{RB(NMe_2)_2 + 3HCl \rightarrow RBCl_2.NHMe_2 + NH_2Me_2Cl}$$

But rupture of a B—N bond of $\mathrm{MeB(NMe_2)_2}$ also occurs if the product of the reaction with HCl is heated:

$$\mathrm{[MeClB(NHMe_2)_2]Cl \xrightarrow{170\text{–}180^\circ C} MeB(Cl)NMe_2 + NH_2Me_2Cl}$$

The homologue $\mathrm{EtB(NMe_2)_2}$ shows both types of reaction with HCl, depending on the conditions. The stability of the salt-like product $\mathrm{[RClB(NHMe_2)_2]Cl}$ is clearly very dependent on the size of the group R. Reaction of compounds of the type $\mathrm{RB(NMe_2)_2}$ with HBr is in all cases analogous, but the methyl analogue reacts with only one molecule of HI in toluene solution:

$$\mathrm{MeB(NMe_2)_2 + HI \rightarrow [Me(Me_2N)B.NHMe_2]I}$$

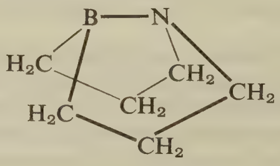
Although the product will not react further with HI, it readily adds on HCl:

$$\mathrm{[Me(Me_2N)B.NHMe_2]I + HCl \rightarrow [MeClB(NHMe_2)_2]I}$$

This is probably because the chloro atom has smaller spatial requirements around the boron atom, so that ligand size again appears to be an important factor: otherwise these compounds in general show the expected chemical properties. With $\mathrm{Fe_2(CO)_9}$ in dioxan, $\mathrm{MeB(NMe_2)_2}$ has been observed to form the unstable orange crystalline adduct $\mathrm{(OC)_3Fe.MeB(NMe_2)_2}$, for which the infrared and ^{11}B n.m.r. spectra suggest π bonding between the $\mathrm{BN_2}$ grouping and the zerovalent iron atom.[465]

Cyclic Boranamines

A particularly interesting boranamine, in which the character of the B—N bond might be somewhat modified, is the bicyclic compound 1-aza-5-borabicyclo[3.3.0]-octane[373, 469]



which can be prepared from diallylamine $\mathrm{NH(CH_2CH{=}CH_2)_2}$ and $\mathrm{H_3B.NEt_3}$ upon cracking the dimer—which is first formed—at *c.* 180°C. The first ionization potential is relatively low.[373] However, the photoelectron spectrum of this compound shows no significant effect which can be unequivocally attributed to reduced π overlapping in the B—N linkage on account of its non-planar environment.[469]

Unsaturated B-Organoboranamines

Examples of mixed boranamines containing organic groups other than simple alkyl attached to the boron have been described, and many are relatively stable. Thus, unlike

$Et_2NB(CH{=}CH_2)_2$,[470] bis(dimethylamino)vinylborane $(Me_2N)_2BCH{=}CH_2$ is a monomeric liquid of b.p. 29°C.[471] The unknown monomer $BH(CH{=}CH_2)(NH_2)$ has been treated theoretically.[472] Alkynyl-substituted aminoboranes such as $(Me_2N)_2BC{\equiv}CMe$[304] and $Et_2NB(C{\equiv}CMe)_2$[473] are however apparently dimeric; at least, they are much less volatile, though the simpler members are distillable without decomposition.[307] Here again, studies of the B—N bond by infrared, ultraviolet and n.m.r. spectroscopy have shown that it has partial double-bond character, although the extent is affected by the nature of the substituents on both the boron and the nitrogen.[473] Aryl-substituted aminoboranes such as Me_2NBPh_2 are mostly essentially monomeric, though aminodiphenylborane itself is a dimer, $(BPh_2NH_2)_2$.[474]

Diborylamines

When the organic groups linked to the boron are simple alkyl groups it has further been possible to obtain related compounds in which two $—BR_2$ groups are attached to the same nitrogen atom. Such compounds are normally monomers. Thus reactive bis(dialkylboryl)amines of types $(R_2B)_2NH$ and $(R_2B)_2NR'$ are prepared from the halogeno compound R_2BX and a disilazane or N-metallated boranamine, or alternatively from the appropriate methylthio compound R_2BSMe and ammonia:[441, 475]

$$(Me_3Si)_2NH + 2R_2BCl \rightarrow (R_2B)_2NH + 2Me_3SiCl$$

$$LiNMeBR_2 + R_2BCl \rightarrow (R_2B)_2NMe + LiCl$$

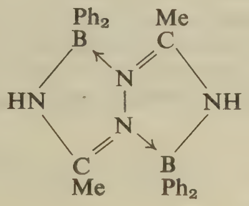
$$2Me_2BSMe + NH_3 \rightarrow (R_2B)_2NH + 2MeSH$$

Other Substituted Boranamines

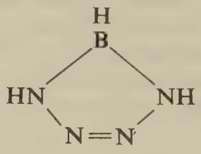
Other characterized aminoboranes with mixed ligands on the boron include $B(NMe_2)_2(GeH_3)$,[337] $B(NMe_2)_2(N_3)$,[476] $B(NMe_2)_2NCO$,[477, 478] $B(NMe_2)_2NCS$,[477, 478] $B(NMe_2)_2(OMe)$,[382] $B(NMe_2)_2(SMe)$,[479] $B(NMe_2)_2(PMe_2)$,[480] $B(NMe_2)_2(AsEt_2)$,[480] $B(NMe_2)_2(SbEt_2)$[480] and $BH(NEt_2)(SMe)$,[481] the last having a vapour pressure of 3 Torr at 0°C and in benzene solution being monomeric—as are the other compounds—notwithstanding the hydrogen atom on the boron; also $B(NMe_2)_2F$,[482, 483] $B(NH_2)Cl_2$ (apparently monomeric in the vapour phase only),[484] $B(NMe_2)_2Cl$,[373] $B(NMe_2)_2BRr$[373] and $B(NMe_2)_2I$,[485] among others, while $B(NMe_2)Cl_2$ exists as a monomer and a dimer.[486] Further examples of dimers are $(BH(NMe_2)Cl)_2$ and $(BH(NMe_2)Br)_2$, with heats of dissociation equal to 30·1 and 42·0 kcal mol^{-1} respectively.[487] Many of the above and related mixed boranes may be prepared by simple redistribution reactions. Examples with three different ligands on the boron, $B(NMe_2)XY$ [X, Y = OR, SMe, F, Cl, Br, I] have been studied.[49] Many are monomeric, as is also definitely established for $BPh(NMe_2)F$.[488]

Apart from the mixed alkyl- and dialkylaminoboranes mentioned above, N-substituted aminoboranes with mixed ligands on the boron include pyridylaminoboranes such as $Ph_2BNH(C_5H_4N)$,[489] acylaminoboranes such as the partly dimerized $Bu_2BNHCOCH_3$,[490] silylaminoboranes such as $Me_2BNH(SiMe_3)$,[491] $PhB(NH_2)(N(SiMe_3)_2)$,[492] $PhB(N(SiMe_3)_2)Cl$[492] and $B(NMe_2)(N(SiMe_3)_2)Cl$,[493–5] germylaminoboranes such as $PhB(NMe_2)(N(GeMe_3)_2)$[492] and stannylaminoboranes such as $Ph_2BNMe(SnMe_3)$[496] and $B(NMe_2)_2(N(SnMe_3)_2)$;[492] also hydrazinoboranes such as $Bu_2BNPhNHPh$[197, 198] and the related bis-borylhydrazine $Ph_2BNHNHBPh_2$, which with two molecules of acetonitrile undergoes an insertion reaction to give an unexpectedly stable product that is probably the bicyclic azine of diphenylborylamino ketone:[497]

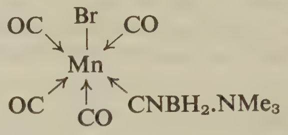
$$Ph_2BNHNHBPh_2 + 2MeCN \longrightarrow$$



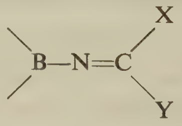
Also to be mentioned here are thiophosphinylaminoboranes such as $Et_2BNMeP(S)Me_2$[498] and thiophosphorylboranes, for example, $Me_2BNMeP(S)(NMe_2)_2$.[498] Cyclic species are also possible: thus the action of azomethane MeN_3 on $H_3B.NH_2Me$ and $H_3B.NH_2Ph$ respectively has produced the 2,5-dimethyl and 2-methyl-5-phenyl derivatives of the unknown cyclotetrazinoborane[499]



Mixed boranes with unsaturated nitrogen directly bonded to the boron include the isocyanoborane adduct with trimethylamine, $Me_3N.BH_2NC$ (m.p. 46–47°C), which in turn can form coordination complexes with metals, as in $Me_3N.BH_2NC.AgCN$ and $BrMn(CO)_4(CNBH_2.NMe_3)$, in which the donor is apparently a carbon atom:[500]



Also to be mentioned here are N-substituted alkylaminoboranes (or N-borylimines)[436] such as $Et_2BN{=}CPh_2$,[501] $(i\text{-}Pr)_2BN{=}CPh(NMe_2)$[502] and $(MeS)_2BN{=}C(SMe_2)$.[503] Compounds containing the grouping



can often be prepared from nitrile-insertion reactions with halogenoboranes R_2BX[504]

$$R_2BX + N{\equiv}CY \rightarrow R_2BN{=}CXY$$

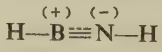
Not all compounds of this type are monomeric, however: for example, $Bu_2BN{=}CCl_2$ is dimeric.[505] Closely related are isocyanato- and isothiocyanatoboranes, e.g. $PhB(N{=}C{=}O)_2$ and $PhB(N{=}C{=}S)_2$,[478, 506] and azidoboranes, e.g. $BMe_2(N_3)$,[507] $BEt(N_3)_2$,[450] $B(NMe_2)_2(N_3)$ and $B(OMe)_2(N_3)$.[476]

Boranes with Doubly Bonded Nitrogen Substituents

Simple compounds with boron doubly bonded to nitrogen are not isolable under ordinary conditions, although they might be expected to have transitory existence. Attempts to prepare them lead to polymeric forms, commonly the trimers, namely derivatives of borazine $B_3N_3H_6$. The simplest representative of this class of compounds, boranimine or iminoborane, $HB{=}NH$, has long been expected[508] to be the first product of thermal decomposition of boranamine

$$H_2B{-}NH_2 \xrightarrow{\text{heat}} HB{=}NH + H_2$$

But only recently has its existence been demonstrated as the major product of photolysis of $H_3B.NH_3$, a proof accomplished by rapid freezing of the HBNH in an argon or xenon matrix.[509] Vibrational frequencies from the infrared spectra of HBNH and isotopic species have enabled the stretching force constant of the B=N bond to be determined as $13{\cdot}14 \times 10^5$ dyn cm^{-1}. The molecule is linear. The radical •BNH was identified at the same time. Prior to its discovery, HBNH had been given theoretical treatments,[510–12] which in part indicate the polarity of the boron-nitrogen bond to be



$$H{-}\overset{(+)}{B}{\equiv}\overset{(-)}{N}{-}H$$

The cyclic dimer, trimer and tetramer have also been studied theoretically,[388, 513–15] and theory furnishes reasons for expecting the dimer to be thermodynamically much less favoured[511] than the trimer, which may explain why the dimer, 1,3,2,4-diazadiboretidine $(BHNH)_2$, has not been observed. Concerning the remarkably stable cyclic trimer, borazine $(BHNH)_3$, see p. 596. The tetramer, octahydro-1,3,5,7,2,4,6,8-tetraazatetraborocine $(BHNH)_4$, is again unknown. Nevertheless, it is long since derivatives of boranimine were first isolated as cyclic dimers[516] and tetramers.[517] Simple alkyl and aryl derivatives, whether of type HBNR, RBNH or RBNR′, are unknown as monomers, although many are well characterized as cyclic trimers and occasionally also as polymers, e.g. $(BHNMe)_x$.[518] In particular it might be expected that the diphenyl derivative Ph—B=N—Ph would be stabilized as a monomeric species through conjugation effects, but it is so far known only as the trimer, hexaphenylborazine $(BPhNPh)_3$.[519]

DERIVATIVES WITH PHOSPHORUS SUBSTITUENTS

Methods have long been known for producing compounds containing B—P bonds.[520] The simpler phosphinoboranes are not monomers, but either oligomers or polymers. In their oligomerization they show differences with respect to the aminoboranes, in that they usually exist as trimers and tetramers and hardly ever as dimers. In this and certain other respects they bear a greater resemblance to the arsinoboranes.

No evidence exists for a monomeric form of the parent phosphinoborane, BH_2PH_2. Attempts to prepare it by heating phosphine borane $H_3B.PH_3$ have led only to a refractory solid:[521]

$$H_3B.PH_3 \xrightarrow{\text{heat}} \frac{1}{n}(H_2BPH_2)_n + H_2$$

On analysis, however, the product was found to be deficient in hydrogen and to have the approximate composition $PBH_{3\cdot75}$. Similarly the product from methylphosphine borane $H_3B.PH_2Me$ is $(H_2BPHMe)_n$, which is however a non-volatile oil. The main product from dimethylphosphine borane $H_3B.PHMe_2$ at 150°C is a mixture of the somewhat volatile solid trimer and tetramer of dimethylphosphinoborane, $(H_2BPMe_2)_3$ and $(H_2BPMe_2)_4$, mainly the former.[521] A little higher polymer is formed at the same time, but the claim to have isolated impure monomeric H_2BPMe_2 as a substance that melted over the 84-degree range 41–125°C(!) and could not be distilled *in vacuo* is based on unsatisfactory evidence and has never been confirmed. The trimers of substituted phosphinoboranes are treated as bridge-substituted derivatives of triborane(9) (see p. 180) and the tetramers as derivatives of a hypothetical cyclic tetraborane of formula B_4H_{12} (p. 226). Other methods of preparing these compounds and their homologues are known. The polymer $(H_2BPMe_2)_x$ is a brittle white translucent solid with an apparently linear structure and a value of x in the neighbourhood of 80.[522] Though insoluble in most solvents, it is soluble in hot benzene and sets to a thick gel on cooling. The analogue $(H_2BPMeEt)_x$ has elastic properties.[522]

When the phosphinoborane is further substituted at the boron, the derivatives may still be oligomers or may be monomers, according to the nature of the substitution. Thus dimethyl(dimethylphosphino)borane is a trimer, $(Me_2BPMe_2)_3$,[521] but Ph_2BPEt_2 (m.p. 192°C) with its bulkier electron-releasing substituents is monomeric.[474] The latter compound was prepared by the reaction

$$BPh_2Cl + LiPEt_2 \xrightarrow[C_6H_6]{25^\circ C} Ph_2BPEt_2 + LiCl$$

The fully phenylated derivative, Ph_2BPPh_2, which can be sublimed *in vacuo* at 240°C, is similar, in that neither compound is hydrolyzed by water, in contrast to substituted boranamines. Nor are these compounds air-sensitive.

No biphosphinoborane of type $HB(PR_2)_2$ is known, but $PhB(PPh_2)_2$ (m.p. 5·5°C) can be prepared:[523]

$$BPhCl_2 + 2PHPh_2 + 2NEt_3 \xrightarrow[C_6H_6]{25^\circ C} PhB(PPh_2)_2 + 2NHEt_3Cl$$

It is monomeric and colourless, but when heated in benzene solution a yellow polymeric form is slowly deposited. It is susceptible to oxidation by the air or by alkaline hydrogen peroxide solution:

$$PhB(PPh_2)_2 + 4H_2O_2 + 2NaOH \rightarrow PhB(OH)_2 + 2Na[Ph_2PO_2] + 4H_2O$$

Trisphosphinoboranes of formula $B(PR_2)_3$ cannot be prepared from B_2H_6 and lithium compounds of type $LiPR_2$ by a method analogous to the preparation of trisaminoboranes $B(NR_2)_3$ from $LiNR_2$ compounds (p. 428), since different products result:[524]

$$LiPMe_2 + B_2H_6 \rightarrow Li[PMe_2(BH_3)_2]$$

But the use of BCl_3 with $LiPEt_2$ has led to the desired product as the dimer $(B(PEt_2)_3)_2$ (m.p. 148°C)[525]

$$6LiPEt_2 + 2BCl_3 \xrightarrow[Et_2O]{-78^\circ C} (B(PEt_2)_3)_2 + 6LiCl$$

Mixed trisubstituted boranes that contain at least one —NR_2 group are readily prepared:[480]

$$LiPMe_2 + B(NMe_2)_2Cl \rightarrow B(NMe_2)_2PMe_2 + LiCl$$

$$2LiPEt_2 + B(NMe_2)Cl_2 \rightarrow B(NMe_2)(PEt_2)_2 + 2LiCl$$

These compounds are monomeric, but unlike BPh_2PMe_2 are exceedingly sensitive with respect to hydrolysis and oxidation.

It is also sometimes possible to obtain boranes in which two boron atoms are linked to the same phosphorus atom, as in the formation of the compound $(Ph_2B)_2PPh$ (m.p. 62–64°C):[523]

$$2BPh_2Cl + PH_2Ph \xrightarrow[C_6H_{14}]{25^\circ C} (Ph_2B)_2PPh + 2HCl$$

This compound is also monomeric and sensitive towards atmospheric oxidation.

DERIVATIVES WITH ARSENIC SUBSTITUENTS

Arsinoboranes contain the B—As bond and closely resemble phosphinoboranes, although in general their thermal stability is slightly lower. The unsubstituted compound prepared from diborane(6) and arsine is a non-volatile polymer $(H_2BAsH_2)_n$:[526]

$$B_2H_6 + 2AsH_3 \xrightarrow[5\,d]{25^\circ C} \frac{2}{n}(H_2BAsH_2)_n + 2H_2$$

but like its phosphorus analogue it is hydrogen-deficient and reportedly more closely approximates to the formula $(BAsH_{3\cdot7})_n$. On heating, more hydrogen is lost. The monomethyl compound $(H_2BAsHMe)_n$ obtained from methylarsine is non-volatile and, as prepared, is also hydrogen-deficient, though to a lesser degree.[526] The dimethyl compound is also not known as a monomer, but has been similarly obtained from dimethylarsine as a trimer, $(H_2BAsMe_2)_3$ (m.p. 49·7–50·6°C), and a less stable tetramer, $(H_2BAsMe_2)_4$ (m.p. 149·5–150·5°C), along with a higher polymer $(H_2BAsMe_2)_n$. They are also formed by gently heating the borane(3) adduct of tetramethyldiarsine in a high vacuum:[527]

$$Me_4As_2.BH_3 \xrightarrow{30\text{–}40^\circ C} \frac{1}{n}(H_2BAsMe_2)_n + AsHMe_2 \qquad [n = 3, 4]$$

The trimer and tetramer are derivatives of B_3H_9 (p. 180) and a hypothetical B_4H_{12} (p. 226) respectively. The polymer resembles the phosphorus analogue, but is much less stable and begins to lose hydrogen at 50°C.[526]

The fully substituted arsinoboranes may or may not be monomeric. Thus the tetramethylated compound, prepared from $Me_3SnAsMe_2$, is a spontaneously inflammable trimer, $(Me_2BAsMe_2)_3$ (m.p. 65°C):[527]

$$3Me_3SnAsMe_2 + 3BMe_2Br \xrightarrow[n\text{-}C_6H_{14}]{25^\circ C} (Me_2BAsMe_2)_3 + 3SnMe_3Br$$

Refs. p. 439

the similarly prepared dimethylarsinodiphenylborane a partly associated monomer, Ph_2BAsMe_2,[527] while the tetraphenyl derivative (m.p. 202–204°C)[474]

$$BPh_2Cl + NaAsPh_2 \xrightarrow[C_4H_8O]{-60°C} Ph_2BAsPh_2 + NaCl$$

and diethylphosphinobis(dimethylamino)borane[480]

$$B(NMe_2)_2Cl + LiAsEt_2 \xrightarrow[Et_2O]{-15°C} (Me_2N)_2BAsEt_2 + LiCl$$

are apparently monomeric. The last-named compound is very susceptible to oxidation and hydrolysis.

The bisarsinoborane $Et_2NB(AsEt_2)_2$ has similarly been prepared:[480]

$$B(NEt_2)Br_2 + 2LiAsEt_2 \xrightarrow[Et_2O]{-75°C} Et_2NB(AsEt_2)_2 + 2LiBr$$

It is likewise monomeric and subject to ready oxidation and hydrolysis.

DERIVATIVE WITH ANTIMONY SUBSTITUENTS

Stibinoborane H_2BSbH_2 is unknown as a monomer or polymer; also stibine SbH_3 does not react with diborane(6) at temperatures below those where it decomposes, except that the decomposition of the stibine appears to be catalytically accelerated by the presence of B_2H_6. This is seen,[528] for example, in the reaction between $NaBH_4$ and $SbCl_3$ in diglyme, in which both gases are produced simultaneously.[529] Monomeric dimethylstibinoborane H_2BSbMe_2, for many years thought to be a product of the interaction of diborane(6) with tetramethyldistibine Sb_2Me_4,[530] has latterly been shown[531] to be based on mistaken evidence and in all probability does not exist.

The only other stibinoborane so far reported is a borane with mixed substituents, namely bis(dimethylamino)diethylstibinoborane $(Me_2N)_2BSbEt_2$, which has been prepared from the dioxane adduct of $LiSbEt_2$:[480]

$$LiSbEt_2.C_4H_8O_2 + B(NMe_2)_2Cl \xrightarrow[Et_2O]{-10°C} (Me_2N)_2BSbEt_2 + LiCl + C_4H_8O_2$$

This compound is monomeric, is very vulnerable to hydrolysis and oxidation and commences to decompose above 0°C with the formation of an antimony mirror.

DERIVATIVES WITH BISMUTH SUBSTITUENTS

No borane containing a B—Bi bond has been described to date. The existence of certain plumbylboranes encourages one to believe that bismuthylboranes should be capable of preparation.

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SECTION B8

CARBORANES

BY R. W. JOTHAM

INTRODUCTION AND NOMENCLATURE

The term 'carborane' is now used as a collective name for those carbon–boron–hydrogen systems in which the carbon atoms form an integral part of the molecular framework. In most cases the carborane may be related to a known or hypothetical borane, and its nomenclature is devised accordingly. The remarkable history of carboranes spans scarcely 15 years, and much of the early work was not declassified until 1963. Since then this fast-growing topic has been covered by more than 500 publications. Only the very early work has been comprehensively reviewed[1], but the reader's attention is drawn to several other important reviews.[2–10] One of these[9] surveys otherwise unpublished data that are available in industrial research reports. A number of short reviews should also be mentioned.[11–20] In addition, there have been published specialist reviews of the transition-metal complexes of carborane anions[21–3] and of carborane polymers[24–5], as well as an important text-book which is principally concerned with a discussion of bonding in boron hydrides and carboranes.[26]

From the time of the pioneer work of Stock[27], it is probable that many early investigators obtained trace quantities of carboranes from hydrocarbon–borane reactions. These products were not characterized until such reactions were extensively studied in the high-energy fuel programmes of countries interested in rocket propulsion. The early results remained classified for a considerable time, so that some of the carboranes were discovered independently. Five pioneer groups should be mentioned: (a) A group studying the reactions of acetylene with pentaborane(9) isolated the smaller carboranes $C_2B_3H_5$, both isomers of $C_2B_4H_6$, $C_2B_4H_8$ and $C_2B_5H_7$ derived respectively from pentaborane(5), hexaborane(6), hexaborane(8) and heptaborane(7).[28–9] (b) Three totally independent groups of workers[30–2] appear to have discovered 1,2-dicarbadodecaborane(12), 1:2-$C_2B_{10}H_{12}$, and its derivatives at about the same time. The first preparation was accredited to Bobinski[13], and used the reaction of isoprenyl acetylene with the bis-acetonitrile derivative of decaborane.[33–4] The product was later shown to be *C-iso*propenyl-1:2-dicarbadodecaborane(12):

$$CH_2{=}C(CH_3){-}C{\equiv}C{-}H + B_{10}H_{12}(CH_3CN)_2 \rightarrow CH_2{=}C(CH_3)C_2B_{10}H_{11} + H_2 + 2CH_3CN$$

Nevertheless, a U.S.A. patent covering the products of the same reaction was also issued.[35]

The fifth pioneer group was concerned with theoretical and structural studies of carboranes.[26,36] A number of papers dealing with the boranes themselves are normally extrapolated to cover the isoelectronic carboranes.[26,36–44] Likewise the structures of hexahydrohexaborate(2−), $B_6H_6^{2-}$, and dodecahydrodecaborate(2−) anion, $B_{12}H_{12}^{2-}$ [45–7] provided important clues to the structures of the $C_2B_4H_6$ and $C_2B_{10}H_{12}$ isomers. An electron population analysis for isomers of $C_2B_3H_5$, $C_2B_4H_6$, $C_2B_5H_7$ and $C_2B_{10}H_{12}$ was published prior to the description of such compounds in the open literature, and eventually proved to be a remarkably accurate prediction of the observed structures. The numbers of possible isomers for various substituted carboranes have been predicted.[48]

Some difficulties in the nomenclature of carboranes have been discussed.[49] The standard nomenclature in current use is based on that used for the boron hydrides themselves[50–2], but alternative nomenclature for dicarbadodecaborane derivatives is used by Russian authors.[53] The standard nomenclature is best illustrated by reference to the known carborane skeletons, which are depicted in Figs. 1–32 in which larger shaded rings serve for carbon atoms, unshaded larger rings are for boron atoms and the smaller circles are for hydrogen atoms disposed in approximately the expected structure.

Closo-carboranes are completely constructed of triangular faces, and they usually contain no bridging hydrogen atoms. Each boron and carbon atom is normally bonded to a single terminal hydrogen atom, while the framework bonds are of the three-centre type.[26] The atoms are numbered in sequential planes perpendicular to the longest, highest-order axis. The atoms in each perpendicular plane are numbered clockwise from a reference plane containing the symmetry axis. The frameworks with an open face do normally include bridging hydrogen atoms, and are termed *nido*-carboranes or *arachno*-carboranes. The prefix *nido*- is derived from the Greek word for nest and *arachno*- from the corresponding word for web; *closo*- has replaced the earlier *clovo*- (Greek, cage) but the reason for this change is obscure.[8] In the *arachno*- and *nido*-carboranes the atoms are numbered from plane projection drawings of the hydride structures viewed from a position opposite to the open portion of the framework. Each set is numbered clockwise from the same reference plane. When the addition of only one atom would produce a *closo*-structure, the numbering for *closo*-structures is used and the position of the 'missing' atom is indicated by a *bracketed* number.[52]

Uncharged carboranes are named according to the corresponding borane, exploiting the *iso*electronic sets CH–BH$^-$ and CH–BH$_2$. Thus a compound of formula $C_2B_3H_5$ is iso-electronic with pentahydropentaborate(2−), $B_5H_5^{2-}$, and is called a *closo*-dicarbapentaborane(5). The possible isomers are distinguished by indicating the positions of the carbon atoms by the prefixes 1:2-, 2:3- or 1:5-. The latter, which is the only one known without substituents, is called *closo*-1:5-dicarbapentaborane(5) and is shown in Fig. 3 to be compared with the 1:2-isomer in Fig. 2. *Nido*-carboranes are iso-electronic with boranes of the general formula B_nH_{n+4}, whereas *arachno*-boranes are iso-electronic with boranes of the B_nH_{n+6} series.

Carborane anions are named in the same way as the corresponding borane anions. Thus the ion $C_2B_4H_7^-$ (Fig. 27) is known as *nido*-4:5-dicarbaheptahydrohexaborate(1−). The CH–BH$_2$ iso-electronic series, in which the borane counterpart includes one terminal and one bridging hydrogen atom, is illustrated by the compounds $C_4B_2H_6$ (Fig. 25), $C_3B_3H_7$ (Fig. 24), $C_2B_4H_8$ (Fig. 20), CB_5H_9 (Fig. 19) and B_6H_{10}. The CH–BH$^-$ series is illustrated by $C_2B_{10}H_{12}$ (Figs. 12, 13, 14), $CB_{11}H_{12}$ (Fig. 18) and $B_{12}H_{12}^{2-}$. Extensive classifications of this type have been listed.[8] The iso-electronic series CH$_2$–BH with all hydrogens terminal is not usually exploited. The elegant basket molecule dimethylenetetraborane shown in Fig. 33 is usually regarded as an alkyl-substituted borane rather than a carborane.[54–5]

A number of trivial names for some of the carboranes may be found in the earlier literature. The reader's attention is drawn to the following alternative names still in current use by some authors. *Nido*-4:5-dicarbahexaborane(8) (Fig. 20) is referred to as *nido*-2:3-dicarbahexaborane(8) in most of the publications to date. Both names select the apical boron as atom 1, i.e. B^1. In the earlier name the pentagonal base of Fig. 20 was numbered so as to minimize the numbers in the prefix. In the present name, numbering is referred to the basal boron atom in the plane of symmetry. In a similar way, the prefix in *nido*-2:3:4-tricarbahexaborane(7) (Fig. 24) has been altered to *nido*-2:3:6-. In the isomeric *nido*-dicarbadodecahydro-undecaborate(1−) ions (Figs. 31–2) the prefixes 1:2- and 1:7- refer to the same compounds as those with the prefixes *nido*-7:8- and *nido*-7:9-. Russian authors call the isomers 1:2-, 1:7- and 1:12-$C_2B_{10}H_{12}$ (Figs. 12–14), *ortho*, *meta*- and *para*-barene respectively.[53]

Earlier 'carborane' was used instead of barene. The *meta*-isomer has also been named *neo*-carborane. Unfortunately some Russian authors use a different numbering system for the boron atoms of 1:2-$C_2B_{10}H_{12}$, although in most Russian papers the system is that shown in Fig. 12. In this review standard nomenclature or an unambiguous empirical formula is adopted, using the numbering systems given in the Figs. 1–32.

The extensive literature on derivatives of carboranes precludes detailed discussion of the many aspects of interest. Instead the known carboranes and their derivatives have been tabulated *in extenso*. Unsubstituted carboranes and their properties are listed in Tables I–IV. When different authors give different values for a physical property for which the most reliable cannot yet be inferred, all the measurements are normally listed, except that only the higher of close melting-points is given, and one selected value is given for the boiling point, refractive index or density.

The analytical techniques in general use for organo-boron compounds[56–9] are satisfactory also for the carboranes. In fact the most powerful techniques for the investigation of carboranes have proved to be high-resolution mass-spectrometry and ^{11}B nuclear-magnetic resonance. Detailed discussions of the application of these techniques have been given.[8, 60]

CARBORANES (5–11 FRAMEWORK ATOMS)

Many of the smaller carboranes and some of their derivatives may be obtained[61] by the reactions of acetylenes with the smaller boranes, especially pentaborane(9). A large number of papers mention the formation of trace amounts of the small carboranes, and discuss their interconversions. Of the preparative methods mentioned in the Tables, those which seem to be most convenient have been selected for specific mention. A number of general papers and conference reports cover the production and characterization of the small carboranes.[28, 62–73] Mention is also made of some definitive patents.[74–5]

Although dicarbacarboranes are usually obtained from acetylenes, only rarely are the two carbon atoms found in adjacent positions. It is therefore important to consider the skeletal rearrangements of carborane systems and those containing 5, 6, 10 and 12 boron atoms have received detailed treatment.[76–7] For the cases of compounds of formulae $C_2B_3H_5$, $C_2B_6H_8$, $C_2B_7H_9$ and $C_2B_9H_{11}$ these rearrangements are considered to proceed through intermediates where two adjacent triangles of the borane fragment become a square with unconnected—in the topological sense—diagonals. Such '*dsd*' rearrangements happen very easily, and for these four systems the carbon atoms may be scrambled between all possible positions. Each of these carborane systems is observed experimentally in only one isomeric form (Figs. 3, 7, 8, 11), namely that isomer in which the carbon atoms have the smallest co-ordination number although alkylated derivatives of 1:2-dicarbapentaborane(5) are also known. For the $C_2B_5H_7$ and $C_2B_8H_{10}$ systems, two '*dsd*' rearrangements must occur in order to scramble the carbon atoms. Repetition enables all possible isomers to be produced. Only one isomer has been observed for dicarbaheptaborane(7) (Fig. 6), but two isomers of dicarbadecaborane(10) are known. The 1:10-$C_2H_8B_{10}$ isomer (Fig. 10) is predicted to be the more stable[78] and 1:6-dicarbadecaborane(10) (Fig. 9) changes quantitatively to this isomer at 350°C.[79] Both possible isomers of dicarbahexaborane(6) and all three possible isomers of dicarbadodecaborane(12) are known (Figs. 4, 5, 12–14). Rearrangements in these systems are much less facile.[77] The octahedral six-atom system might rearrange *via* a trigonal-prismatic intermediate. The '*dsd*' intermediate for the twelve-atom systems is thought to be a cube-octahedron.[80] Such an intermediate suffices for the rearrangement of 1:2-$C_2B_{10}H_{12}$ to 1:7-$C_2B_{10}H_{12}$ observed at 450°C[81], but the 1:12-isomer cannot be obtained by repetition of this process. The *para*-isomer is obtained in small yield at 630°C, presumably *via* a much more open intermediate. One possibility involves the 120° rotation of a single face. Isomeric species are less common for the *nido*-carboranes, but two isomers of each of the formulae $C_2B_9H_{13}$, $C_2B_9H_{12}^-$ and $C_2B_9H_{11}^{2-}$ are known (Figs. 22, 23, 29–32). The rearrangements of these systems closely parallel those of the *closo*-dicarbadodecaboranes.

Disproportionation reactions of the smaller carboranes occur fairly readily, and have found synthetic applications. These reactions account for the simultaneous formation of several carboranes even in optimum preparative methods. Thus $C_2B_4H_8$, $C_2B_5H_7$, both isomers of $C_2B_4H_6$ and 1:5-$C_2B_3H_5$ are usually formed together in the reaction of acetylene with pentaborane(9). Pyrolysis of $C_2B_7H_{13}$ has led to the preparation of both known isomers of $C_2B_8H_{10}$ as well as $C_2B_7H_9$ and $C_2B_6H_8$.[79] The yield of the dicarbadecaborane(10) isomers was much improved by co-pyrolysis with diborane(6).

Discussion of individual carboranes and their derivatives follows. The *closo*-dicarbadodecaboranes have a derivative chemistry which by far exceeds that of all other carboranes and is deferred to p. 471.

Closo-Carboranes

CLOSO-1-CARBAHEXABORANE(7) CB_5H_7 (Fig. 1)

Closo-carbahexaborane(7) is prepared from methylpentaborane(9) using the silent electric discharge.[82–4]

$$CH_3B_5H_8 \rightarrow CB_5H_7 + 2H_2$$

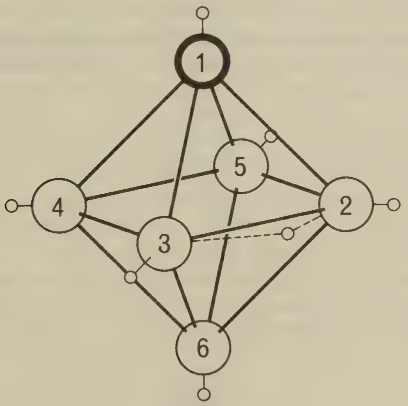


FIG. 1

The structure was established from the ^{11}B n.m.r. spectrum[82] which shows three doublets in the intensity ratio 2:2:1 at 19·1, 9·7 and −2·5 p.p.m. with respect to an external boron trifluoride diethyletherate reference. The B–H coupling constants are 184, 162 and 174 Hz respectively. No derivatives have yet been reported.

OTHER *CLOSO*-MONOCARBORANES

The zwitterion compounds $CB_{10}H_{10}[N(CH_3)_3]$ and $CB_{10}H_{10}[N(CH_3)_2n\text{-}C_3H_7]$ have been described[85] (Table V).

CLOSO-1:2-DICARBAPENTABORANE(5) 1:2-$C_2B_3H_5$ (Fig. 2)

The parent carborane is not known at present, but[86–8] a number of *B*- and *C*-methylated derivatives have been prepared by the reaction of diborane with acetylenes in a silent electric discharge. *C*:3-$(CH_3)_2$-1:2-$C_2B_3H_3$ appears to be the derivative of this carborane which is most readily obtained. The known derivatives are listed in Table VI.

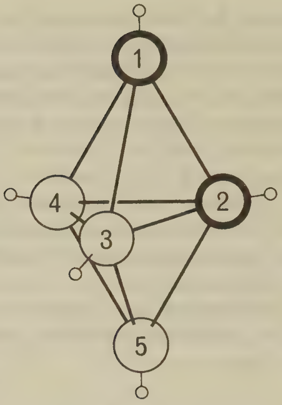


FIG. 2

CLOSO-1:5-DICARBAPENTABORANE(5) 1:5-$C_2B_3H_5$ (Fig. 3)

This compound is readily obtained in about 40% yield by the rapid high-temperature pyrolysis of *nido*-4:5-dicarbahexaborane(8).[61] Co-pyrolysis of $C_2B_4H_8$ with trimethylborane(3) greatly increases the yield of $C_2B_3H_5$ at the expense of other carboranes.[89] $C_2B_3H_5$ may also be obtained from $C_2B_4H_8$ by u.v. irradiation[90], and is obtained in smaller quantities by a number of other methods.[9, 29, 86–8, 91–6] Its structure was established from the simple doublet in the ^{11}B n.m.r. spectrum[28], which has since received intensive study.[8] References to other properties of this compound including the ^1H n.m.r., infra-red and mass-spectra are given in Table I.

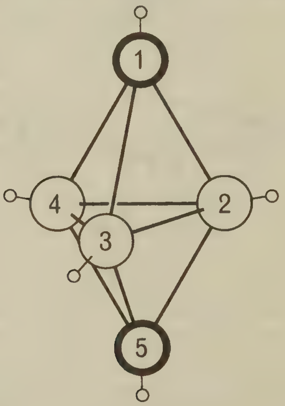


FIG. 3

Several derivatives of 1:5-$C_2B_3H_5$ have been described and are listed in Table VI. The synthesis of numerous peralkyl derivatives of the small carboranes has been described.[5] In most cases the characterization of these compounds or their isomeric mixtures does not appear to be complete, and the reported empirical formulae only are given. The peralkyl-dicarbapentaborane(5) compounds are also listed in Table VI.

1:5-$C_2B_3H_5$ decomposes at 150°C to liberate hydrogen and form tan-coloured solids.[92] It does not react with acetone, carbon dioxide, air or water at room temperature. Only the hydrogen atoms attached to boron exchange with the deuterium atoms of hexadeuterodiborane(6).[29]

CLOSO-1:2-DICARBAHEXABORANE(6) 1:2-$C_2B_4H_6$ (Fig. 4)

The best method for the preparation of the 1:2-$C_2B_4H_6$ isomer appears to be u.v. irradiation of the *nido*-carborane $C_2B_4H_8$[90, 94]: a 15% yield is obtained, while smaller amounts have been obtained by other methods.[61,89,92,95,97] The structure has been established from the presence of two overlapping doublets of equal intensity in the ^{11}B n.m.r. spectrum[8,28], and by microwave studies.[68] At 250°C it rearranges to the 1:6-isomer.[92] References to other properties including ^{1}H n.m.r., i.r. and u.v. spectra are given in Table I. Derivatives are listed in Table VII.

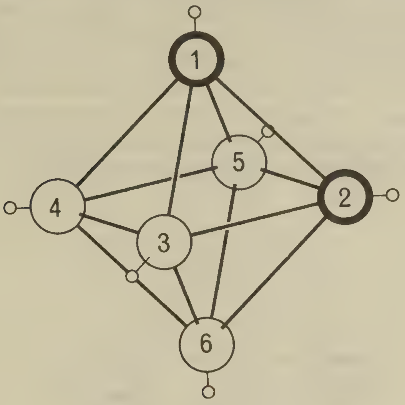


FIG. 4

CLOSO-1:6-DICARBAHEXABORANE(6) 1:6-$C_2B_4H_6$ (Fig. 5)

The *trans*-isomer of dicarbahexaborane(6) is more readily available than the *cis*-isomer and more derivatives are known. It is obtained in 20% yield by pyrolysis of *nido*-4:5-$C_2B_4H_8$ at 450°C for 1–3 seconds.[61] A 20% yield is also obtained by u.v. irradiation of this *nido*-carborane.[90] The preparation of 1,6-$C_2B_4H_6$ is described in several other publications.[9,87,89,91–5,97–8] Its structure has been established from the single doublet at 19·4 p.p.m. ($J_{B-H} = 189$ Hz) in the ^{11}B n.m.r. spectrum.[8,28] It does not react with acetone, trimethylamine, ammonia, air or water at room temperature. The hydrogen atoms attached to boron exchange slowly with hexadeuteroborane(6).[97] References to other properties including ^{1}H n.m.r., i.r. and mass-spectra and vapour pressure are given in Table I. Carbon- and boron-substituted derivatives have been reported[87,91,93], as well as isotopic variants[91] and the peralkyl compound $(C_2H_5)_4(CH_3)_2C_2B_4$.[63] These are listed in Table VII.

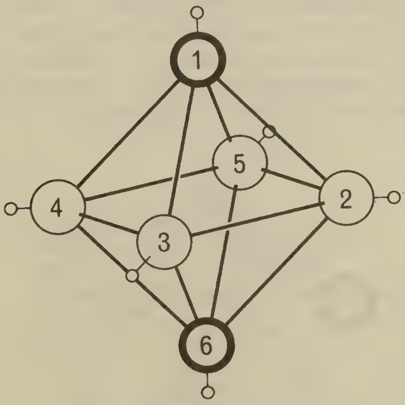


FIG. 5

CLOSO-2:4-DICARBAHEPTABORANE(7) 2:4-$C_2B_5H_7$ (Fig. 6)

Dicarbaheptaborane(7) is the most easily obtained of the *closo*-carboranes with less than 12 framework atoms.[8] It is prepared in 40% yield by pyrolysis of $C_2B_4H_8$.[61]

It is obtained in smaller yield by the reaction of pentaborane(9) and acetylene in the silent electric discharge.[29,97] The preparation of this compound has been described also by other authors.[28,86–7,89,91–5,98–9] The structure was originally established from the ^{11}B n.m.r. spectrum[91], which contains three doublets in the ratio 2:2:1 and it was confirmed by microwave investigations.[100–2] Strict planarity of the pentagon has not been established.[10] The dipole moment was found to be $4{\cdot}41 \times 10^{-30}$ C m (1·32 D).[101] The interatomic distances to within ±0·005 nm are as follow[100]: B^1—C^2 = 0·1708, B^1—B^3 = 0·1818, B^1—B^5 = 0·1815, C^2—B^3 = 0·1546, C^2—B^6 = 0·1563, B^5—B^6 = 0·1651, B–H = 0·120, C–H = 0·109 nm. References to other properties are given in Table I. A number of derivatives of $C_2B_5H_7$ are listed in Table VIII. Of the peralkyl derivatives of the small carboranes, the compound $(C_2H_5)_5(CH_3)_2C_2B_5$ has been studied in greatest detail.[63,103–8]

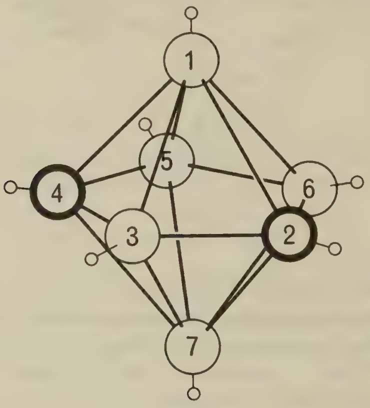


FIG. 6

CLOSO-1:7-DICARBAOCTABORANE(8) 1:7-$C_2B_6H_8$ (Fig. 7)

Closo-dicarbaoctaborane may be prepared in 30% yield by pyrolysis of $C_2B_7H_{13}$ in diphenyl ether at 200°C.[79,99,109,110] The *C,C′*-dimethyl derivative has also been produced by reaction of hexaborane(10) with acetylene promoted by u.v. irradiation.[78] The structure has been inferred from the two doublets in the intensity ratio 4:2 in the ^{11}B n.m.r. spectrum.[8] The few known derivatives are listed in Table IX. The *C*:*C′*-dimethyl derivative, $C_2(CH_3)_2B_6H_6$, is more readily available than the parent molecule[78–9,99,111–12], and has been the subject of *X*-ray studies which establish the structure of the parent molecule.[113–14] Similar studies of *C*-substituted derivatives have arisen for other carborane systems, because *X*-ray data are normally unable to distinguish between C–H and B–H groups.

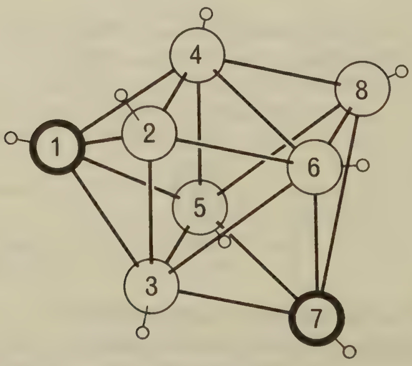


FIG. 7

CLOSO-4:5-DICARBANONABORANE(9) 4:5-$C_2B_7H_9$ (Fig. 8)

Closo-dicarbanonaborane is prepared by a degradation of 2:3-$C_2B_9H_{11}$ which is oxidized to $C_2B_7H_{13}$ in 70% yield by chromic acid.[115] When the *nido*-dicarbanonaborane(13) is pyrolyzed in diphenyl ether at 200°C, 4:5-$C_2B_7H_9$ is obtained in 7% yield.[99, 109, 112] Its structure was established from the three doublets in the ratio 1:2:4 in the ^{11}B n.m.r. spectrum.[79] The few known derivatives are listed in Table X. The structure of the *C*:*C'*-dimethyl derivative has been determined by *X*-ray investigation.[116]

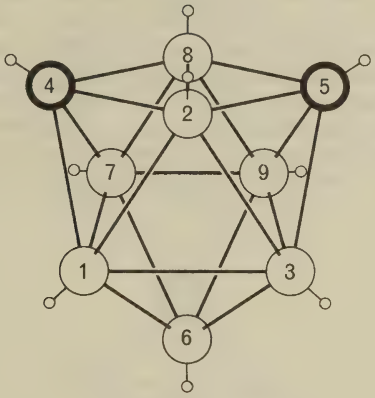


FIG. 8

CLOSO-1:6-DICARBADECABORANE(10) 1:6-$C_2B_8H_{10}$ (Fig. 9)

Both isomers of *closo*-dicarbadecaborane(10) are prepared from $C_2B_9H_{11}$ *via* $C_2B_7H_{13}$. The 1:6-isomer is obtained in 30% yield by pyrolysis of $C_2B_7H_{13}$ in diphenyl ether at 200°C.[79, 93, 98–9, 109, 112] The yield is increased to 40% in presence of diborane.[79] Small quantities have also been obtained by pyrolysis of $C_2B_4H_8$.[89] The structure has been inferred from the complex ^{11}B n.m.r. spectrum.[8] 1:6-$C_2B_8H_{10}$ and its derivatives are quantitatively converted to the corresponding 1:10-isomers by pyrolysis at 350°C.[79] A number of derivatives are listed in Table XI.

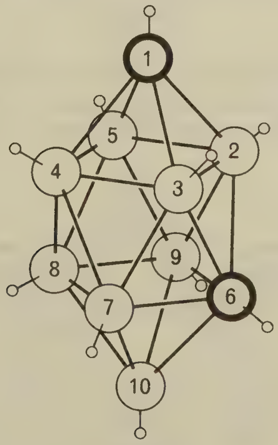


FIG. 9

CLOSO-1:10-DICARBADECABORANE(10) 1:10-$C_2B_8H_{10}$ (Fig. 10)

1:10-$C_2B_8H_{10}$ is obtained quantitatively from the 1:6-isomer by pyrolysis at 350°C.[79, 112, 117] Its structure has been established from the single doublet at 10·3 p.p.m. ($BF_3.O(C_2H_5)_2 = 0{\cdot}0$), ($J_{B-H} = 162$ Hz) in the ^{11}B n.m.r. spectrum.[8, 79] A number of derivatives are listed in Table XI. The carbon atoms in 1:10-$C_2B_8H_{10}$ uniquely occupy the positions of lowest coordination number. In consequence, it has been predicted to be the most stable *closo*-carborane of all[78], and indeed it has been found to be substantially more stable to basic degradation than the $C_2B_{10}H_{12}$ isomers.[109] Although the parent molecule is not yet available in quantity, it seems likely that extensive synthetic chemistry will be developed in this system. Some interesting carbon-substituted derivatives of 1:10-$C_2B_8H_{10}$ have been prepared.[118] When 2:3-$C_2B_9H_{11}$ is treated with *n*-butyllithium, the ion 4-C_4H_9-(3),1,7-$C_2B_9H_{11}^-$ is obtained (N.B. See p. 451 for an explanation of the parenthesized numbers). If this reaction is carried out in presence of 1:10-$C_2B_8H_{10}$, the ion 4-(1:10-$C_2B_8H_9$)-(3):1:7-$C_2B_9H_{11}^-$ is obtained, with a direct B–C bond linking the two carborane units. The corresponding ethyl-substituted derivative is shown in Fig. 34. If the product is treated with polyphosphoric acid, a hydride-ion-abstraction reaction occurs, giving the neutral compound 4-(1:10-$C_2B_8H_9$)-2:3-$C_2B_9H_{10}$. The influence of the inductive effect in both *closo*-dicarbadecaborane(10) systems has been discussed.[117]

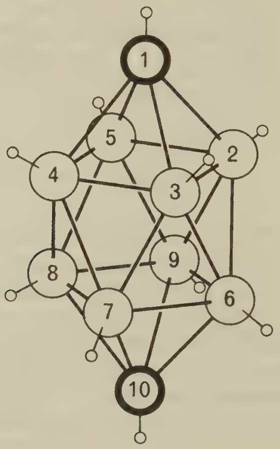


FIG. 10

CLOSO-2:3-DICARBAUNDECABORANE(11) 2:3-$C_2B_9H_{11}$ (Fig. 11)

1:2-$C_2B_{10}H_{12}$ and 1:7-$C_2B_{10}H_{12}$ are both quantitatively degraded to the corresponding $C_2B_9H_{12}^-$ isomers by sodium methoxide.[119] On neutralization with acid

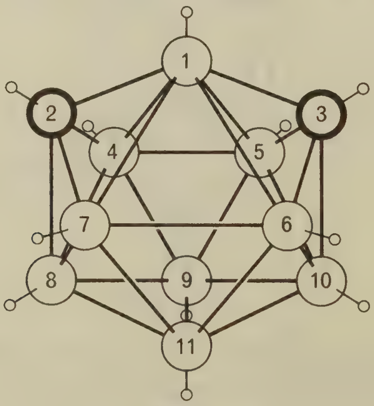


FIG. 11

the two isomeric *nido*-carboranes of formula $C_2B_9H_{13}$ are obtained. Both of these isomers give 2:3-$C_2B_9H_{11}$ in 22% yield on pyrolysis above 100°C.[111] When the $C{:}C'$-dimethyl derivatives are involved, the final yield is 75%.[120] Several derivatives are listed in Table XII.[121] A series of 4-substituted derivatives of 1:7-$C_2B_9H_{12}^-$ have been converted to the corresponding 4-substituted derivatives of 2:3-$C_2B_9H_{11}$

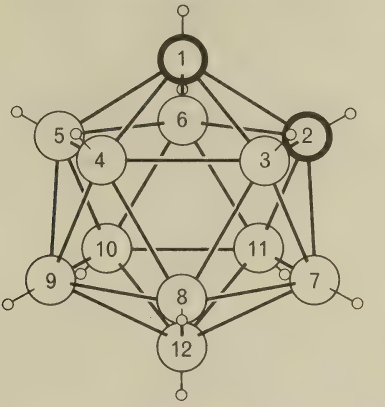


FIG. 12

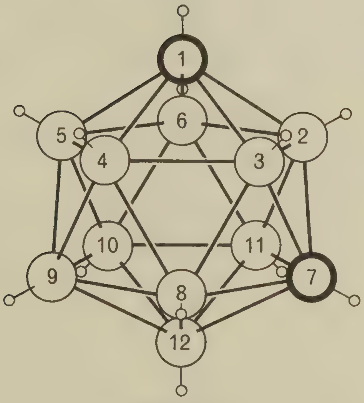


FIG. 13

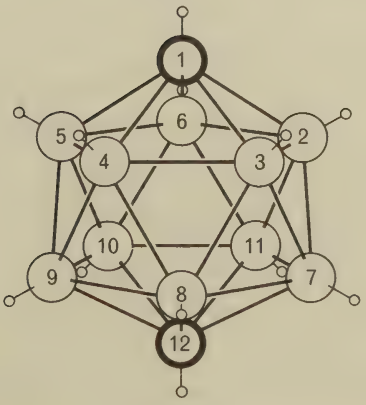


FIG. 14

with polyphosphoric acid.[118] The substituents include methyl-, dicyanomethyl-, 1:2-$C_2.CH_3.B_{10}H_{10}$ (Fig. 35) and 1:10-$C_2HB_8H_8$. *X*-ray investigation[122] has established the structure of the *C*,*C′*-dimethyl derivative of 2:3-$C_2B_9H_{11}$.

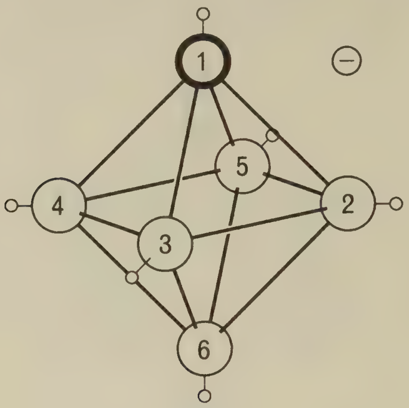


FIG. 15

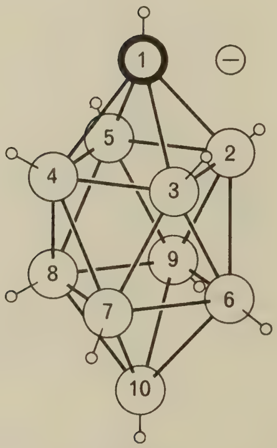


FIG. 16

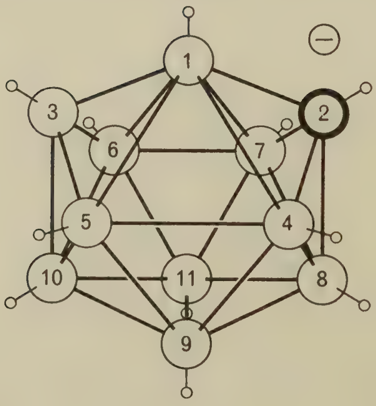


FIG. 17

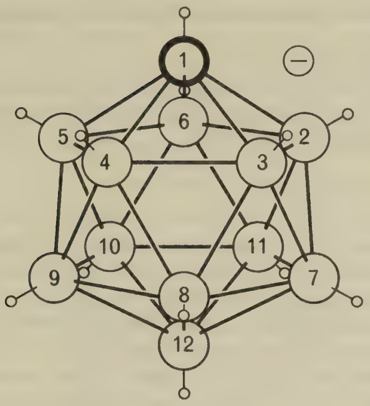


FIG. 18

ALKYL DERIVATIVES OF *CLOSO*-CARBORANES

Alkyl groups appear to stabilize *closo*-carborane frameworks with respect to isomerization or disproportionation. Examples are the $C,B\text{-}(CH_3)_2\text{-}1\!:\!2\text{-}C_2B_3H_3$ compounds[123], where one of the carbon atoms remains in a position of higher coordination number despite a potentially facile '*dsd*' rearrangement to the 1:5-isomer. $C_2B_3(CH_3)_2(C_2H_5)_3$ can be distilled at 170°C[67], whereas *closo*-1:5-dicarbapentaborane(5) itself decomposes at 150°C. This distinction may provide an important clue to the synthesis of presently unknown skeletal isomers.[8] The following reactions have been used for the preparation of peralkyl *closo*-carboranes[63, 89, 103–4, 124–6]:

$$(C_2H_5)_2BCl + Li \xrightarrow{\text{tetrahydrofuran}} C_2(CH_3)_2B_3(C_2H_5)_3, C_2(CH_3)_2B_5(C_2H_5)_5$$

$$B_2H_2(C_2H_5)_4 + C_2H_2 \xrightarrow[\text{heat}]{\text{pressure}} C_2(CH_3)_2B_n(C_2H_5)_n$$

$$B_2H_x(C_2H_5)_{6-x} \xrightarrow{\text{heat}} C_2(CH_3)_2B_n(C_2H_5)_n$$

$$LiC{\equiv}CCH_3 + (C_2H_5)_2BF,N(CH_3)_3 \xrightarrow{-\text{LiF}}$$

$$CH_3C{\equiv}C{-}B(C_2H_5)_2,N(CH_3)_3 \xrightarrow{BF_3,OR_2}$$

$$(C_2H_5)_2BC{\equiv}CCH_3 \xrightarrow{B_2H_2(C_2H_5)_4} C_2(CH_3)_2B_3(C_2H_5)_3\ (52\%)$$

$$C_2B_4H_8 \xrightarrow{B(CH_3)_3,\ 340°C} C_2H_2B_5(CH_3)_5\ (+\text{other } B\text{-methyl derivatives})$$

$$C_2B_4H_8 \xrightarrow{B(CH_3)_3,\ 600°C} C_2H_2B_3(CH_3)_3\ (+\text{other } B\text{-methyl derivatives})$$

CLOSO-CARBORANE ANIONS

Some unsubstituted *closo*-carborane anions are listed in Table II. *Closo*-hexahydro-1-carbahexaborate(1−), $CB_5H_6^-$ (Fig. 15), is obtained from CB_5H_7 by hydride abstraction of the bridging hydrogen atom.[83] The preparation of the anions $1\text{-}CB_9H_{10}^-$, $2\text{-}CB_{10}H_{11}^-$, and $1\text{-}CB_{11}H_{12}^-$ (Figs. 16–18) from amine derivatives of *nido*-carboranes has been described. The structures of these ions have been established from the ^{11}B n.m.r. spectra.[127] The zwitterion compound $CB_{10}H_{10},N(CH_3)_3$[85] is probably a derivative of the $2\text{-}CB_{10}H_{11}^-$ ion. Some further derivatives of *closo*-carborane anions, shown in Table XIII, have been described recently.[128–9] In these compounds the carborane unit appears to be σ-bonded to a metal. An example is $1\!:\!10\text{-}C_2[Fe(CO)_2(\pi\text{-}C_5H_5)]_2B_8H_8$.[128] The structure of $(C_2B_9H_{10})_2Co(S_2CH)$, shown in Fig. 36, has been established by *X*-ray investigation[129], while the related anion $(C_2B_9H_{10})_2CoS_2^-$ was also reported.

Nido-Carboranes and *Arachno*-Carboranes

NIDO-1-CARBATETRABORANE(7) 1-CB_3H_7

The peralkyl compound $(C_2H_5)_6CH_3CB_3$ and the compound illustrated in Fig. 37 have been described.[130] It is interesting that neither the parent carborane nor the parent borane, B_4H_8, appears to be stable.

NIDO-2-CARBAHEXABORANE(9) 2-CB_5H_9 (Fig. 19)

The parent carborane, 2-CB_5H_9, has been obtained from $C_2B_6H_8$ by treating with dry HCl the solid product obtained from $C_2B_6H_8$ by reaction with tetramethylammonium tetrahydroborate. A number of alkyl derivatives of this *nido*-carborane have been obtained as by-products during the preparation of $C_2B_4H_8$.[132–4] The peralkyl compound $(C_2H_5)_5CH_3CB_5H_3$ has been obtained as a by-product of the hydroboration of acetylene by tetra-ethyl diborane.[107] Derivatives of all the *nido*-monocarboranes are listed in Table XIV, apart from amine derivatives which are discussed collectively below. *Nido*-2-carbahexaborane(9) is part of a series terminating with *nido*-hexaborane(10).

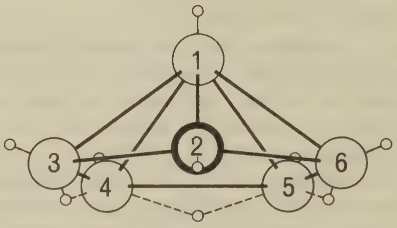


FIG. 19

NIDO-4:5-DICARBAHEXABORANE(8) 4:5-$C_2B_4H_8$ (Fig. 20)

Nido-4:5-dicarbahexaborane(8), often referred to as *nido*-2:3-dicarbahexaborane-(8), is obtained in 40% yield by the co-pyrolysis of pentaborane(9) and acetylene at 235°C.[92] It is thus one of the most readily available carboranes.[135–7] Its structure was originally established from the three doublets in the ratio 2:2:1 in the ^{11}B n.m.r. spectrum[78, 138], which has been the subject of much study.[8, 92, 139–44] The structure was confirmed by *X*-ray investigations of the *C*:*C*′-dimethyl derivative.[145–6] Isotopic exchange with deuterium and hexadeuterodiborane(6) has been studied in detail.[147] Numerous[148–50] derivatives are listed in Table XV. The following bond distances have been given[145] for the dimethyl derivative: B^1—C^4, 0·1762; B^1—B^3, 0·1768; B^1—B^2, 0·1705; C^4—C^5, 0·1432; C^4—B^3, 0·1520; and B^2—B^3, 0·1778 nm. The pyrolysis of $C_2B_4H_8$ is used to prepare 1:5-$C_2B_3H_5$, 1:6-$C_2B_4H_6$ and 2:4-$C_2B_5H_7$.[61] Subjecting $C_2B_4H_8$ to the silent electric discharge[29] or u.v. irradiation[90] yields these compounds and the 1:2-isomer of $C_2B_4H_6$, which is not so readily obtained. This carborane is also a member of the *nido*-hexaborane(10) series.

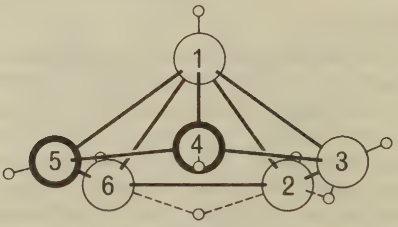


FIG. 20

ARACHNO-1:3-DICARBANONABORANE(13) 1:3-$C_2B_7H_{13}$ (Fig. 21)

When the *closo*-carborane 2:3-$C_2B_9H_{11}$ is treated with chromic acid[115], $C_2B_7H_{13}$ is obtained as a degradation product. The preparation of this compound has been described by other authors.[111–12, 151] The structure of $C_2B_7H_{13}$, which belongs to the nonaborane(15) family, cannot be established unambiguously from the ^{11}B n.m.r. spectrum[8], but it was demonstrated by *X*-ray study of the *C*:*C′*-dimethyl derivative.[152] A number of derivatives are listed in Table XVI. Pyrolysis of $C_2B_7H_{13}$ in diphenyl ether at 200°C is used to prepare the *closo*-carboranes 1:7-$C_2B_6H_8$, 4:5-$C_2B_7H_9$, 1:6-$C_2B_8H_{10}$ and, indirectly, 1:10-$C_2B_8H_{10}$.[79, 99, 109–10]

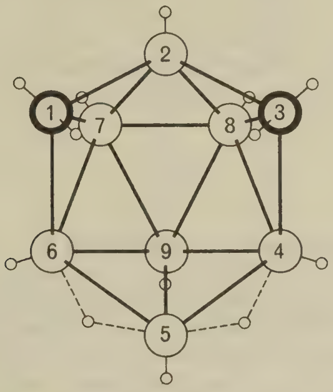


FIG. 21

NIDO-(3):1:2-DICARBAUNDECABORANE(13) (3):1:2-$C_2B_9H_{13}$ (Fig. 22)

This compound has been prepared by neutralization of the related (3):1:2-$C_2B_9H_{12}^-$ ion[120, 153], which is obtained by degradation of 1:2-$C_2B_{10}H_{12}$ with a base. Some substituted *nido*-dicarbaundecaborane(13) compounds are listed in Table XVII. Rather more numerous amine complexes are discussed later. The (3) in the systematic name indicates the position of the abstracted boron atom. This *nido*-carborane is *iso*electronic with undecaborane(15), $B_{11}H_{15}$.

(3)

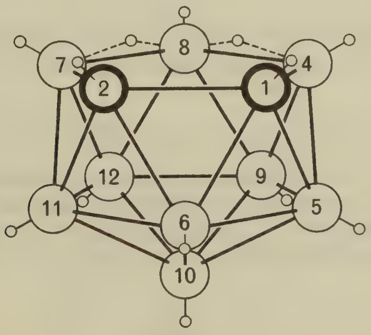


FIG. 22

NIDO-(3):1:7-DICARBAUNDECABORANE(13) (3):1:7-$C_2B_9H_{13}$ (Fig. 23)

The 1:7-isomer of $C_2B_9H_{13}$ is prepared by neutralization of (3):1:7-$C_2B_9H_{12}^-$.[120, 153] Both isomers of $C_2B_9H_{13}$ give 2:3-$C_2B_9H_{11}$ when heated[120] and the same products are obtained by oxidation.[154] They can be titrated as monoprotic acids in aqueous methanol.[153]

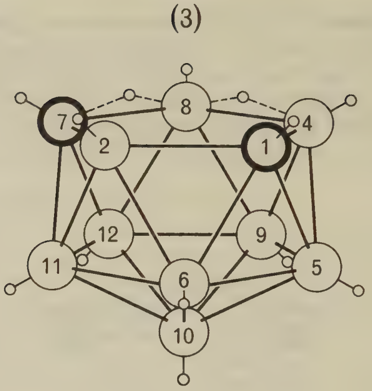


FIG. 23

NIDO-2:3:6-TRICARBAHEXABORANE(7) 2:3:6-$C_3B_3H_7$ (Fig. 24)

The unsubstituted *nido*-2:3:6-$C_3B_3H_7$ has not yet been prepared, but *C*-methyl and dimethyl derivatives may be prepared by the low temperature reaction of tetraborane and acetylene.[98, 123, 132] The structure has been established from the ^{11}B n.m.r. spectrum.[123] A peralkyl derivative has also been described.[63] Some derivatives are listed in Table XVIII. A deuterium tracer study, in which 3:6-$(CH_3)_2$-μ-D-$C_3B_3H_4$ was prepared, has been carried out to locate the position of the bridging hydrogen atom.[155] This carborane is another member of the *nido*-hexaborane(10) series.

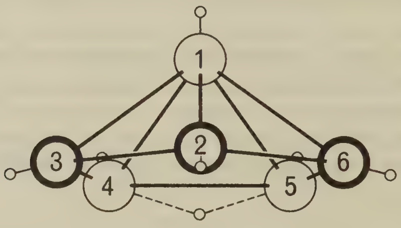


FIG. 24

NIDO-3:4:5:6-TETRACARBAHEXABORANE(6) 3:4:5:6-$C_4B_2H_6$ (Fig. 25)

Peralkyl derivatives of $C_4B_2H_6$ are listed in Table XIX. They can be prepared by the reaction[63, 156]:

$$\mathrm{Na(R_3BC{\equiv}CR) + R_2BCl \rightarrow R_3B{-}C{=}C{-}BR_3 \xrightarrow{\text{trace alkylborane}} C_4B_2R_6.}$$

The structure has been established from the two doublets in the ^{11}B n.m.r. spectrum.[156] The perphenyl derivative has also been described.[157–8] The *closo*-structure assigned to this compound[157] is probably incorrect, because it is evidently yet another member of the *nido*-hexaborane(10) series.

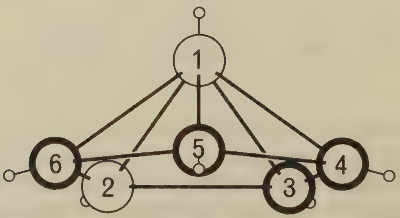


FIG. 25

NIDO-CARBAOCTAHYDROHEXABORATE(1 −) $CB_5H_8^-$ and *ARACHNO*-CARBADECAHYDROHEXABORATE(1 −) $CB_5H_{10}^-$

Some peralkyl derivatives of these ions have been reported, namely $CB_5CH_3(C_2H_5)_5H_2^-$ and $CB_5CH_3(C_2H_5)_5H_4^-$.

$$CB_5CH_3(C_2H_5)_5H_3 \xrightarrow{NaBH(C_2H_5)_3} CB_5CH_3(C_2H_5)_5H_2^- + CB_5CH_3(C_2H_5)_5H_4^- .^{159}$$

The structure is uncertain, but $CB_5H_8^-$ is likely to be derived from *nido*-1-carbahexaborane(9).

NIDO-CARBATRIDECAHYDROUNDECABORATE(1 −) $CB_{10}H_{13}^-$ (Fig. 26)

The preparation of the $CB_{10}H_{13}^-$ ion from the reaction of cyanide ion with decaborane(14) has been described[127]:

$$\begin{aligned} Na_2B_{10}H_{13}CN &\xrightarrow{H^+} CB_{10}H_{12}{:}NH_3 \\ &\xrightarrow[HO^-]{(CH_3)_2SO_4} CB_{10}H_{12}{:}N(CH_3)_3 \\ &\xrightarrow{Na/C_4H_8O} CB_{10}H_{13}^- + 2CB_{10}H_{11}^- \end{aligned}$$

Pyrolysis of $CB_{10}H_{13}^-$ at 310°C gives two anionic *closo*-carboranes, $CB_9H_{10}^-$ and $CB_{11}H_{12}^-$. Some derivatives of $CB_{10}H_{13}^-$ are listed in Table XX. The $CB_{10}H_{11}^{3-}$ ion and isoelectronic $CB_{10}H_{10}$ amine^{2-} ions (see below) have been reported.[160–1]

$$CB_{10}H_{11}^- + 2Na \xrightarrow{C_4H_8O} CB_{10}H_{11}^{3-} + H_2$$

(3)

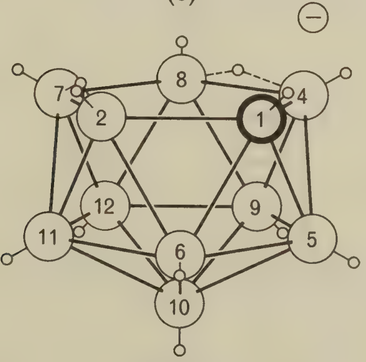


FIG. 26

NIDO-4:5-DICARBAHEPTAHYDROHEXABORATE(1 −) 4:5-$C_2B_4H_7^-$ (Fig. 27)

Sodium hydride abstracts a bridging proton from 4:5-$C_2B_4H_8$ in ether.[162] The $C{:}C'$-dimethyl derivative has been prepared similarly[155]:

$$C_2B_4H_8 + NaH \xrightarrow{(C_2H_5)_2O} C_2B_4H_7^- + Na^+ + H_2$$

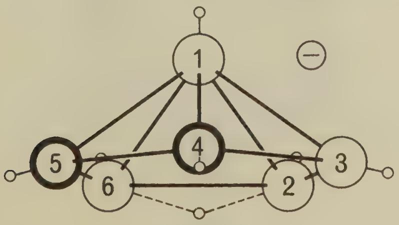


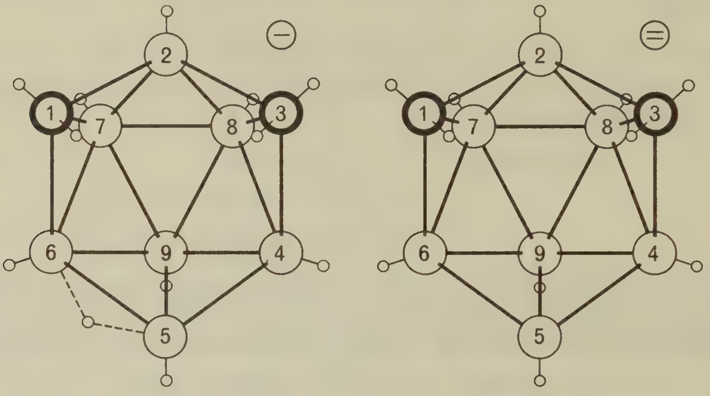
FIG. 27

ARACHNO-1:3-DICARBAUNDECAHYDRONONABORATE(2−), 1:3-$C_2B_7H_{11}^{2-}$ AND *ARACHNO*-1:3-DICARBADODECAHYDRONONABORATE(1−), 1:3-$C_2B_7H_{12}^-$ (Fig. 28)

When the *arachno*-carborane $C_2B_7H_{13}$ is treated with sodium hydride in ether, two protons are abstracted[163]:

$$C_2B_7H_{13}+2NaH \xrightarrow{(C_2H_5)_2O} C_2B_7H_{11}^{2-}+2Na^++2H_2$$

Some derivatives[164] of this ion including the associated 1:3-$C_2B_7(CH_3)_2H_{10}^-$ ion[116, 165], are listed in Table XX.



(a) (b)

FIG. 28

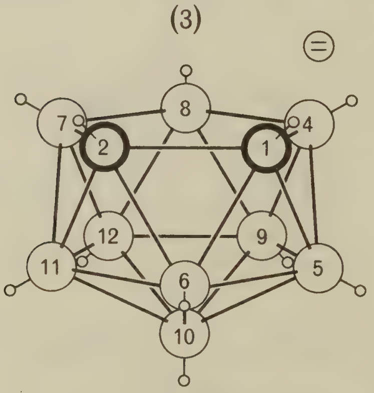


FIG. 29

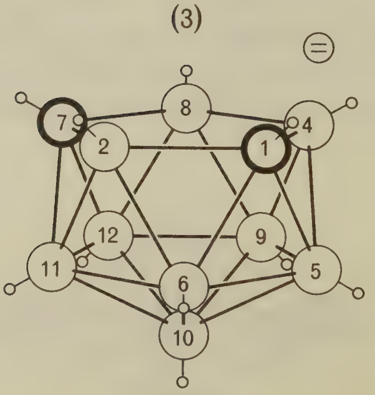


FIG. 30

NIDO-(3):1:2-DICARBADODECAHYDROUNDECABORATE(1−), (3):1:2-$C_2B_9H_{12}^-$ (Fig. 31)

When 1:2-$C_2B_{10}H_{12}$ is treated with a strong base[119, 153, 166–7], the boron atom in the 3-position is removed:

$$C_2B_{10}H_{12} + RO^- + 2ROH \rightarrow B(OR)_3 + H_2 + C_2B_9H_{12}^-$$

X-Ray studies (see p. 469) have established the structure of the two isomeric $C_2B_9H_{11}^{2-}$ ions, but the position of the twelfth bridging hydrogen atom is uncertain. It is presumed to reside on the open pentagonal face.[168] The compounds obtained when the base used is an amine are discussed on p. 470 below. Quite apart from these, several *B*- and *C*-substituted derivatives have been described.[169] These are listed in Table XXI. The *C*-substituted ions (3):1:2-$C_2(CH_3)C_6H_5B_9H_{10}^-$ and (3):1:2-$C_2HC_6H_5B_9H_{10}^-$ have been optically resolved.[119]

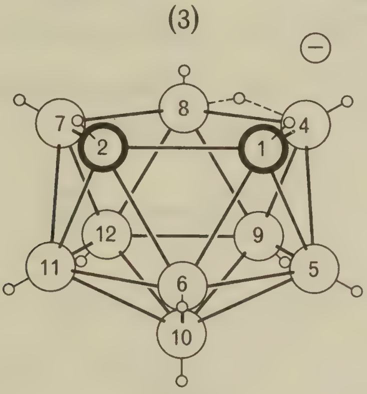


FIG. 31

NIDO-(3):1:7-DICARBADODECAHYDROUNDECABORATE(1−), (3):1:7-$C_2B_9H_{12}^-$ (Fig. 32)

This compound is prepared from the *closo*-carborane 1:7-$C_2B_{10}H_{12}$ in the same way as the 1:2-isomer[170–1], although degradation occurs less readily.[119, 151] The two isomeric ions differ in that the 1:7-isomer has the two carbon atoms in the open face separated by one boron atom. Fewer derivatives have been reported (Table XXII). The anion (3):1:7-$C_2H(C_6H_5)B_9H_{10}^-$ has been optically resolved. The caesium salt of this particular derivative has also been prepared by an isomerization

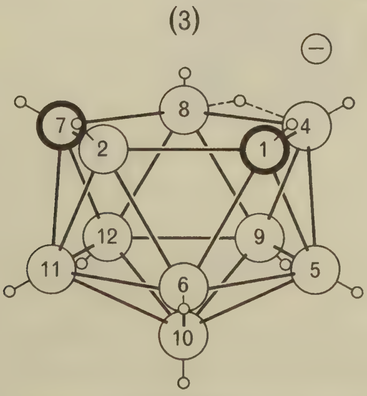


FIG. 32

reaction, consequent upon heating the corresponding 1:2-isomer. Protonation of the $C_2B_9H_{12}^-$ isomers leads to the formation of the two corresponding isomers of $C_2B_9H_{13}$.[120,153] The destructive bromination of 1:2-$C_2B_9H_{12}^-$ ions to vicinal dibromo-compounds has been studied.[172-3] Both isomers are completely degraded by chromic acid.[174]

Some unusual interesting 4-substituted derivatives of (3):1:7-$C_2B_9H_{12}^-$ have been made.[118,175] When 2:3-$C_2B_9H_{11}$ is treated with *n*-butyllithium, the ion 4-(C_4H_9)-(3):1:7-$C_2B_9H_{11}^-$ is obtained, which can be isolated as its tetramethylammonium salt. 4-(CH_3)-(3):1:7-$C_2B_9H_{11}^-$ is prepared similarly. Other species which readily form a lithium salt can be introduced into the 4-position in this way[175]:

$$C_2B_9H_{11} \xrightarrow[LiC_4H_9]{CH_2(CN)_2} 4\text{-}[(CN)_2CH]\text{-}(3)\text{:}1\text{:}7\text{-}C_2B_9H_{11}^-$$

$$\xrightarrow[LiC_4H_9]{CH_2(COOCH_3)_2} 4\text{-}[(CH_3OOC)_2CH]\text{-}(3)\text{:}1\text{:}7\text{-}C_2B_9H_{11}^-$$

$$\xrightarrow[LiC_4H_9]{1\text{:}2\text{-}C_2HCH_3B_{10}H_{10}} 4\text{-}[1'\text{-}(B_{10}H_{10}C_2CH_3)]\text{-}(3)\text{:}1\text{:}7\text{-}C_2B_9H_{11}^-$$

$$\xrightarrow[LiC_4H_9]{1\text{:}10\text{-}C_2HC_2H_5B_8H_8} 4\text{-}[1'\text{-}(1\text{:}10\text{-}B_8H_8C_2C_2H_5)]\text{-}(3)\text{:}1\text{:}7\text{-}C_2B_9H_{11}^-$$

The last compound's structure is shown in Fig. 34.

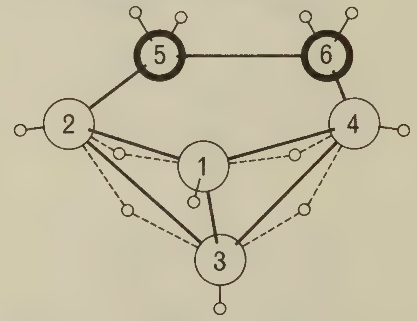


FIG. 33

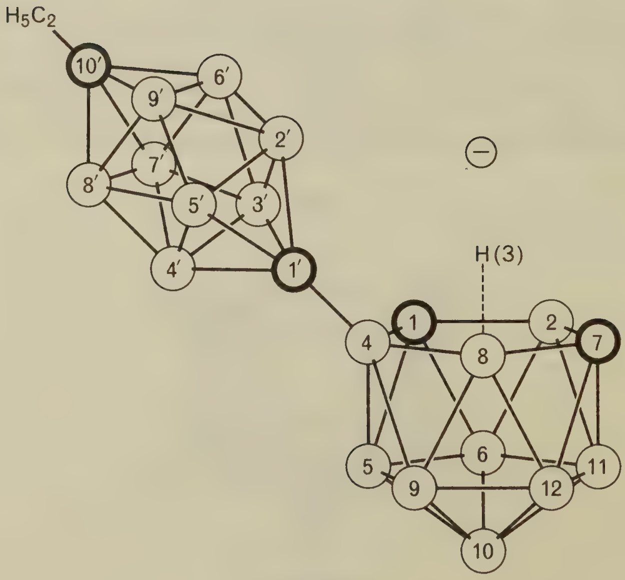


FIG. 34

In the presence of polyphosphoric acid, the ions are converted to the corresponding 4-substituted derivatives of 2:3-$C_2B_9H_{11}$ shown in Fig. 35[118]:

$$B_{10}H_{10}C_2CH_3—C_2B_9H_{11}^- \xrightarrow[\text{acid}]{\text{polyphosphoric}} 4\text{-}[1'\text{-}(1\!:\!2\text{-}B_{10}H_{10}C_2CH_3)]\text{-}2\!:\!3\text{-}C_2B_9H_{10}$$

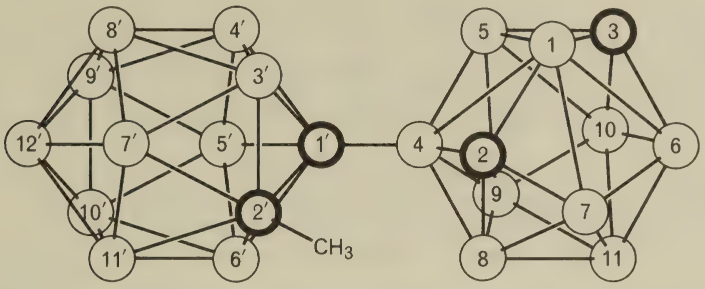


FIG. 35

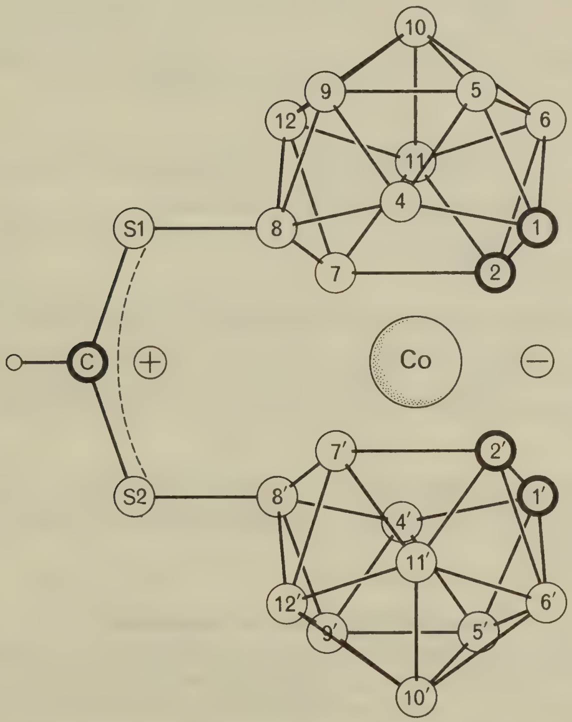


FIG. 36

NIDO-(3):1:2-DICARBAUNDECAHYDROUNDECABORATE(2−), (3):1:2-$C_2B_9H_{11}^{2-}$ AND *NIDO*-(3):1:7-DICARBAUNDECAHYDROUNDECABORATE(2−), (3):1:7-$C_2B_9H_{11}^{2-}$ (Figs. 29, 30)

The $C_2B_9H_{13}$ isomers are very strong acids, and a second proton may be removed from the $C_2B_9H_{12}^-$ ions by reaction with sodium or sodium hydride[176-9]:

$$C_2B_9H_{12}^- + NaH \rightarrow C_2B_9H_{11}^{2-} + Na^+ + H_2$$

Refs. p. 561

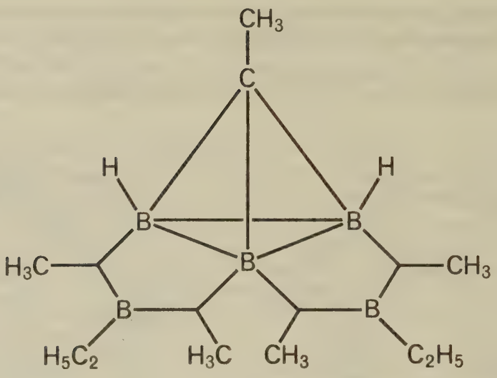


FIG. 37

These ions have been given the name dicarbollides, a word apparently originating in the Spanish name 'olla' for an open icosahedral vessel.[23] The pentagonal open face of either ion $C_2B_9H_{11}^{2-}$ is formally analogous to the isoelectronic *cyclo*pentadienide, $C_5H_5^-$, ion. The electronic properties of all four anions derived from the $C_2B_9H_{13}$ isomers have been discussed.[180] An extensive series of transition-metal complexes developed by Hawthorne and his co-workers is discussed on p. 490. Other derivatives of these ions are listed in Table XXIII.

NIDO-DICARBAOCTAHYDROOCTABORATE(2−), $C_2B_6H_8^{2-}$, *NIDO*-DICARBANONAHYDRONONABORATE(2−), $C_2B_7H_9^{2-}$ AND *ARACHNO*-DICARBADECAHYDRODECABORATE(4−), $C_2B_8H_{10}^{4-}$

Transition-metal complexes of these ions are described on p. 490. They have not otherwise been isolated.

NIDO-1:2-DICARBADODECAHYDRODODECABORATE(2−), 1:2-$C_2B_{10}H_{12}^{2-}$

This ion has not been isolated, but a number of *C*-substituted derivatives have been described.[181–3] These are listed in Table XXIV. The $C_2RR'B_{10}H_{10}^{2-}$ ions are produced by reactions of the $C_2B_{10}H_{12}$ carboranes with alkali metals in liquid ammonia solution.

NIDO-TRICARBAHEXAHYDROHEXABORATE(1−), $C_3B_3H_6^-$

The ion 2:6-$(CH_3)_2$-2:3:6-$C_3B_3H_4^-$ has been obtained by proton abstraction from $(CH_3)_2C_3B_3H_5$.[184]

Amine Derivatives of *Nido*-carboranes

A number of amine adducts of 1:2-$C_2B_{10}H_{12}$ were mentioned in early papers on this carborane.[185–6] It now seems probable that these reports were wrong in detail, because later workers[186–8] report the abstraction of a boron atom by hydrazine or strong amines. The resulting compounds may be formulated as 'onium' salts or zwitterion complexes. For example:

$$C_2B_{10}H_{12} + C_5H_{10}N \rightarrow \overset{\delta-}{C}_2B_9H_{13}\text{—}\overset{\delta+}{N}C_5H_{10} \text{ or } C_5H_{10}NH^+C_2B_9H_{12}^-$$

In presence of excess of amine, one additional molecule of piperidine crystallizes out with this compound.[187–8]

Analogous *C*-substituted derivatives are also known. A list of compounds of the general formula $C_2B_9H_{13}$,L and their derivatives is given in Table XXV. The interesting cyclic zwitterion complexes $C_2B_9H_{11}(CH_2NH_2)_2$ and $C_2B_9H_{12}$[CH2N-

$(C_2H_5)_2]$ are known. In addition, $C_2B_9H_{10}(CH_2NH_2)_2^-$ has been isolated as the triphenylmethylphosphonium salt[189]:

$$1{:}2\text{-}B_{10}H_{10}C_2(CH_2Br)_2 \xrightarrow{NH_3} C_2B_9H_{12}(CH_2NH_2)_2$$

Numerous complexes of the general formula $C_2B_9H_{11},L$ and derivatives of these are listed in Table XXVI.[190-1] A number of complexes of this type have been isolated by treating both $C_2B_9H_{12}^-$ isomers with iron(III) chloride in the presence of a ligand.[190-1] The resulting products appear to carry the attached ligand on one of the three boron atoms of the open pentagonal face. Generally a symmetric and an asymmetric isomer were obtained. This strongly suggests that the ligands are bound directly to the framework.[192-3]

Some *nido*-monocarborane complexes of the series CB_9H_{11},L[127] $CB_{10}H_{12},L$[194-5] are listed in Table XXVII. The complexes of the series $CB_{10}H_{10},L$ described on p. 453 are assumed to be *closo*-carborane derivatives of a similar kind.[85] Decaborane(14) reacts directly with alkyl isocyanides to give compounds of the type $RNH_2\text{–}CB_{10}H_{12}$[196]:

$$B_{10}H_{14}+RNC \rightarrow RNH_2\text{—}CB_{10}H_{12}$$

The reaction of the $B_{10}H_{13}CN^{2-}$ ion with alkyl iodides in tetrahydrofuran produces a mixture of $B_{10}H_{12}CNH_nR_{3-n}$ derivatives.[197] $B_{10}H_{12}CN(CH_3)_3$ and $B_9H_{11}\text{-}CN(CH_3)_3$ have been reported[127]:

$$\begin{aligned} Na_2B_{10}H_{13}CN &\xrightarrow{H^+} B_{10}H_{12}CNH_3 \\ &\xrightarrow{(CH_3)_2SO_4+OH^-} B_{10}H_{12}CN(CH_3)_3 \\ NaB_{10}H_{12}CN,S(C_2H_5)_2 &\xrightarrow{H^+} B_{10}H_{11}OH.CNH_3 \\ &\xrightarrow{(CH_3)_2SO_4+OH^-} B_{10}H_{11}OH.CN(CH_3)_3 \\ &\xrightarrow{OH^-+C_4H_8O} B_9H_{11}CN(CH_3)_3 \end{aligned}$$

The optimum conditions for the preparation of $B_{10}H_{12}C,NH_2C_3H_7$, $B_{10}H_{12}C,\text{-}N(CH_3)_3$ and $B_{10}H_{12}C,NH_3$ have been given.[198]

CLOSO-DICARBADODECABORANES

General Remarks

Closo-1:2-dicarbadodecaborane(12) is the carborane which is most readily available. It is obtained by the reaction of acetylene with decaborane(14) in the presence of a Lewis base:

$$B_{10}H_{14}+C_2H_2 \xrightarrow{\text{Lewis base}} 1{:}2\text{-}C_2B_{10}H_{12}+2H_2$$

Unlike the majority of boron hydrides, it is stable towards water, air and heating to at least 400°C, at which temperature isomerization to the 1:7-isomer begins.[30-2, 35, 186] An alternative preparation is the reaction of the bis-ligand derivative of decaborane(14) directly with acetylene:

$$B_{10}H_{12},L_2+C_2H_2 \rightarrow 1{:}2\text{-}C_2B_{10}H_{12}+H_2+2L$$

Lewis bases such as methyl cyanide, dialkyl sulphides—especially diethyl sulphide, dimethylacetamide, dimethylaniline, tributylphosphine and tetrahydrofuran have been used. The yield with trimethylamine is poor.[31] Carbon-substituted derivatives may be prepared by changing the alkyne used.[199] Alkyl-, aryl-, halogeno-alkyl-, carbalkoxy- and acetoxyalkyl-substituted alkynes may be used. Alcohols and carboxylic acids tend to decompose the boron substrate, but the desired product can often be obtained by saponification of the corresponding carborane ester. Biscarboranes can be obtained from diacetylenes.[200] The $1{:}2\text{-}C_2B_{10}H_{11}$ nucleus behaves like a strongly electron-withdrawing aromatic system with $\sigma^* = 2{\cdot}64$[201], and an extensive derivative chemistry has been developed accordingly utilizing standard organic reactions. This chemistry forms the body of this section and the associated Tables (XXVIII–XXX) provide a summary of the present knowledge: it must be admitted, however, that the list of some 1400 derivatives cannot be regarded as complete. Early patents were issued for the preparation of a wide range of derivatives of 1:2-$C_2B_{10}H_{12}$; hydrocarbons[35,202–7]; *C*-halogen derivatives[208]; alcohols and phenols[209–15]; aldehydes and ketones[216]; carboxylic acids, amides and their derivatives[209,217–22]; esters[223–5]; ethers[226]; miscellaneous derivatives[227–30]; bis-carboranes[231–2]; carborane polymers[233–5]; and for derivatives of 1:7-$C_2B_{10}H_{12}$.[236–7] The separation of derivatives of 1:2-$C_2B_{10}H_{12}$ on silica-gel has been investigated in detail.[238] In general these derivatives have stability and inertia comparable with those of conventional aromatic compounds, and they are therefore conveniently handled by similar techniques.

Numerous workers[26,31,76,81,239–42] suggested that 1:2-$C_2B_{10}H_{12}$ has a geometry close to icosahedral, as is found for the dodecahydrododecaborate(2−) ion.[46] The structure was established by *X*-ray investigations of 1:2-$C_2H_2B_{10}H_2Cl_8$[243–4], and $B_{10}H_{10}C_2(CH_2Br)_2$[245–6]; the conclusions of some earlier workers[247] concerning this compound are now generally regarded as erroneous.[246] Some derivatives are: $B_{10}H_{10}C_2H$—$C_2HB_{10}H_{10}$[248], 9-$B_{10}H_9BrC_2H_2$[249], 9:12-$B_{10}H_8Br_2C_2H_2$[249–50], 8:9:12-$B_{10}H_7Br_3C_2H_2$[249,251], 8:9:10:12-$B_{10}H_6Br_4C_2(CH_3)_2$[249,252], 12-$B_{10}H_9IC_2H$-C_6H_5[253], $B_{10}H_{10}C_2C_6H_5HgBr$[254], $B_{10}H_{10}C_2C_6H_5HgCH_3$[254] and $(B_{10}H_{10}C_2C_6H_5)_2$-Hg.[254] Electron-diffraction studies have been made of $B_{10}H_{10}C_2H_2$[255] and $B_{10}H_{10}$-$C_2(CH_3)_2$.[256] The tendency of the carborane $C_2H_{10}H_{12}$ to form small *C*:*C′*-exocyclic rings[186,240,257–60] suggests strongly that the carbon atoms are adjacent. The presence of a direct C—C bond has been shown by degradation methods.[172,261–4] The C—C bond length is 0·164–0·170 nm (1·64–1·70 Å) which has no parallel in the whole of organic chemistry.[7] If 1:2-$C_2B_{10}H_{12}$ is degraded by alcoholic potassium hydroxide[153] or hydrazine hydrate[186,264], salts of $C_2B_9H_{12}^-$ are obtained; the 1:7-isomer is less easily degraded.[81] If the 1-*iso*propenyl derivative of 1:2-$C_2B_{10}H_{12}$ is heated under reflux in methanol, water, or methanol saturated with hydrogen chloride, it can be recovered unchanged.[31] It can be recrystallized from concentrated sulphuric acid after heating to 150°C. Alkaline potassium permanganate in acetone oxidizes the alkenyl side-group, but does not affect the carborane nucleus.[31,186] Chromic acid, acyl peroxides and hypochlorous acid have little effect on the carborane nucleus.[186,240,257] Nevertheless, $B_{10}H_{10}C_2(COOH)_2$ is completely degraded by alkaline permanganate.[186] The carborane 1:2-$C_2B_{10}H_{12}$ rearranges to 1:7-$C_2B_{10}H_{12}$ at 470°C[81,241], probably *via* a cube-octahedron intermediate.[76,80] The *para*-isomer 1:12-$C_2B_{10}H_{12}$ is obtained from 1:7-$C_2B_{10}H_{12}$ by pyrolysis at 600°C.[265–6] Conversely, 1:7-$C_2B_{10}H_{12}$ is converted to the 1:2-isomer by acid hydrolysis of the 1—1 adduct with sodium[81], or sodium naphthalene derivatives[267–8], and a similar rearrangement of 1:12-$C_2B_{10}H_{12}$ to 1:7-$C_2B_{10}H_{12}$ in liquid ammonia has been reported.[269] These rapid reactions therefore appear to obey Ostwald's law of successive transformations. Hydrogen–deuterium exchange between derivatives of 1:2-$C_2B_{10}H_{12}$ and 1:7-$C_2B_{10}H_{12}$ has been studied.[270] The structure of the 1:7-isomer of $C_2B_{10}H_{12}$ was established by *X*-ray investigation of H—$CB_{10}Cl_{10}C$—H[271] 9:10-H—$CB_{10}H_8Br_2C$—H[272] and 9-H—$CB_{10}H_9IC$—H.[273] Apart from numerous *C*-substituted derivatives of the dicarbadodecaboranes, *B*-substituted derivatives have been obtained by, for example, electrophilic halogenation[185], nitration[274] or boron-insertion reactions of the $C_2B_9H_{12}^-$ ions.[275]

Extensive tabulations of the derivatives of the *closo*-dicarbadodecaborane(12) isomers are presented on pp. 508–556. The more important aspects are discussed below. The individual parent carboranes listed in Table I are discussed on p. 473.

The Taft σ^* value for the 1:2-$C_2B_{10}H_{11}^-$ nucleus has been estimated variously as 3·0–3·5 and 2·64[201,265], similar to that of the strongly electron-withdrawing groups such as chloride, fluoride and cyanide. The pK_a values for the carboxylic acids $B_{10}H_{10}C_2CH_3.COOH$, CH_3—$CB_{10}H_{10}C$—COOH and 1:12-$B_{10}H_{10}C_2H.COOH$ are

2·8, 3·1 and 3·6 (in 50% aqueous ethanol) respectively.[81,276] These, and other similar data in Tables XXVIII–XXX, confirm the electron-withdrawing power of the carborane nuclei, which appears to decline through the series *ortho* > *meta* > *para*. There is also extensive chemical evidence for this electron-withdrawing power[31,186,240,259], which has been closely investigated. This is exemplified by the facile C—C bond cleavage in the carboxylic acid and ketone derivatives by bases[277–9], and evidence for 'positive' iodine atoms in the *C*-iodo derivatives of 1:7-$C_2B_{10}H_{12}$.[280] ^{19}F n.m.r. spectra have been used to study the effect of solvents on the electronic properties of the 1:2-, 1:7- and 1:12-$C_2B_{10}H_{11}^-$ groups.[281]

There are some extensive compilations of 'finger-print' infra-red spectra of carborane derivatives.[282–3] A comprehensive list of n.m.r. data available up to 1965 has been compiled.[1]

***Closo*-dicarbadodecaborane(12) Isomers**

CLOSO-1:2-DICARBADODECABORANE(12), 1:2-$C_2B_{10}H_{12}$ (Fig. 12)

1:2-Dicarbadodecaborane(12) has generally been prepared in up to 70% yields from the reaction of decaborane with acetylene in the presence of methyl cyanide or diethyl sulphide.[30–1] An alternative method is the reaction of the bis-ligand adduct of decaborane with acetylene:

$$B_{10}H_{14} + 2L \xrightarrow{-H_2} B_{10}H_{12},L_2 \xrightarrow{C_2H_2} 1{:}2\text{-}C_2B_{10}H_{12} + H_2 + 2L; \quad L = CH_3CN,(C_2H_5)_2S$$

Decaborane is expensive, but a cheap new synthesis of $B_{10}H_{12}[S(C_2H_5)_2]_2$ has been developed[284–5]:

$$(C_2H_5)_4NBH_4 \xrightarrow{185°C} B_{10}H_{10}^{2-} \xrightarrow[HCl]{(C_2H_5)_2S} B_{10}H_{12}[S(C_2H_5)_2]_2$$

The preparation of 1:2-$C_2B_{10}H_{12}$ is described by many other workers[81,186,286–8], and full details have been given.[289,290] Although the pure crystals melt at 320°C, slight traces of impurity can lower this figure to 285°C.

The dipole moment has been variously measured as 14·4 (4·31)[291], 14·6 (4·39)[292], 14·8 (4·45)[293], 14·9 (4·49)[294], and 15·1 × 10^{-30} C m (4·53 D).[295] Detailed i.r., ^{11}B-n.m.r. and mass-spectra have been given by several workers.[8,81,185,241,249,260,282,296–9] The natural isotopic-distribution ^{13}C-n.m.r. spectra have been reported[300–1], and part of the Raman spectrum has been studied recently.[302] The structure has been directly established from electron-diffraction measurements.[255] The standard heat of formation is −170 kJ mole^{-1} (−40·6 kcal mole^{-1}).[303]

CLOSO-1:7-DICARBADODECABORANE(12), 1:7-$C_2B_{10}H_{12}$ (Fig. 13)

The *ortho*-isomer, 1:2-$C_2B_{10}H_{12}$, has been converted to the 1:7-isomer in 90% yield by heating in the gas phase at 470°C for several hours.[81,236] An almost quantitative yield is obtained by heating at 600°C for 30 s.[259] The preparation has been described by other authors[9,109,304], and the actual rate of formation in isomerization reactions has been studied.[305] The dipole moment has been found to lie in the range 9·2–9·3 × 10^{-30} C m (2·76–2·78 D).[291,293,295] Detailed i.r. ^{11}B-n.m.r., and mass-spectra have been given by several authors from which the structure may be readily inferred.[8,81,241,249,282,296,297,304] Natural-isotopic ^{13}C n.m.r. spectra have been reported[300–1], and the Raman spectrum has been studied recently.[302]

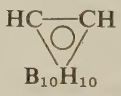
CLOSO-1:12-DICARBADODECABORANE(12), 1:12-$C_2B_{10}H_{12}$ (Fig. 14)

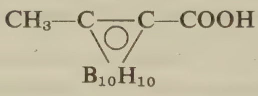
The 1:12-isomer of $C_2B_{10}H_{12}$ is most efficiently prepared in up to 20% yields by heating 1:7-$C_2B_{10}H_{12}$ at 700°C for a few seconds[259,265–6,306], and the kinetics of this reaction have been studied.[305] Detailed spectroscopic data are available.[8,265,296–7] The structure may be inferred for example from the single doublet in the ^{11}B spectrum. The zero dipole moment of this highly symmetrical molecule, point-group D_{5d}, has been demonstrated experimentally.[295,307]

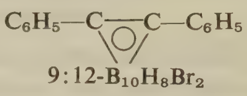
Derivatives of *Closo*-1:2-dicarbadodecaborane(12)

This subject encompasses about two-thirds of the research papers on carboranes published to date. Although American authors were amongst the pioneers of this work[30–1, 35], the most extensive contributions have come from the Russian group led by L. I. Zakharkin and V. I. Stanko.[32] The numerous derivatives are listed in Table XXVIII. These have been classified by the functional groups present but ambiguous cases are mentioned twice. To represent the parent molecule or its derivatives such as 1-methyl-2-carboxy-1:2-dicarbadodecaborane(12) and 1:2-diphenyl-9:12-dibromo-1:2-dicarbadodecaborane(12), two alternative nomenclatures in the Tables or text can be used as appropriate. For example, the following pairs are equivalent:

$B_{10}H_{10}C_2H_2$ $\quad$ $B_{10}H_{10}C_2CH_3.COOH$ $\quad$ $9{:}12\text{-}B_{10}H_8Br_2C_2(C_6H_5)_2$







CARBON-SUBSTITUTED DERIVATIVES

Alkyl, Aryl, Haloalkyl and Ester Derivatives of $1{:}2\text{-}C_2B_{10}H_{12}$

These compounds have been prepared by direct synthesis from decaborane and a substituted acetylene in the presence of a Lewis base. Some typical preparative equations are given below:

$$CH_3C{\vdots}CH + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2HCH_3 + 2H_2 \quad (30,\ 31,\ 308)$$

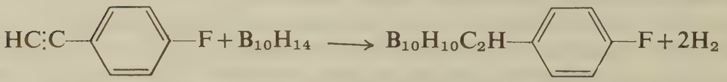
$$CH_2{:}CCH_3.C{\vdots}CH + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2H.CCH_3{:}CH_2 + 2H_2 \quad (30,\ 31)$$

$$C_6H_5C{\vdots}CC_6H_5 + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2(C_6H_5)_2 + 2H_2 \quad (31,\ 287)$$

$$CH_3C{\vdots}C(C_4H_9) + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2CH_3.C_4H_9 + 2H_2 \quad (287)$$

$$HC{\vdots}C.CH_2Cl + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2H.CH_2Cl + 2H_2 \quad (199,\ 309)$$

$$BrCH_2.C{\vdots}C.CH_2Br + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2(CH_2Br)_2 + 2H_2 \quad (31,\ 309)$$

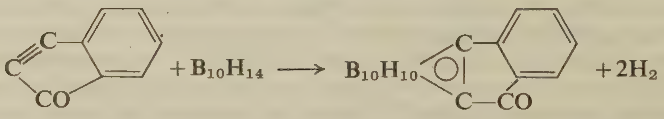


(281, 310)

$$HC{\vdots}C.OC_2H_5 + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2H.OC_2H_5 + 2H_2 \quad (311)$$

$$HC{\vdots}C.COOC_2H_5 + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2H(COOEt) + 2H_2 \quad (312)$$

$$CH_3COOCH_2.C{\vdots}C.CH_2OOCCH_3 + B_{10}H_{14} \rightarrow B_{10}H_{10}C_2(CH_2OOCCH_3)_2 + 2H_2 \quad (30)$$



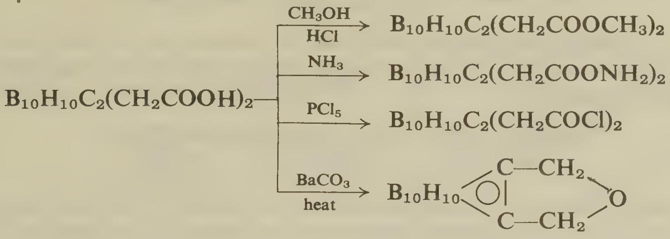
(312–13)

$$HC{\vdots}C.C{\vdots}CH + 2B_{10}H_{14} \rightarrow B_{10}H_{10}C_2H\text{—}C_2HB_{10}H_{10} + 3H_2 \quad (200,\ 248)$$

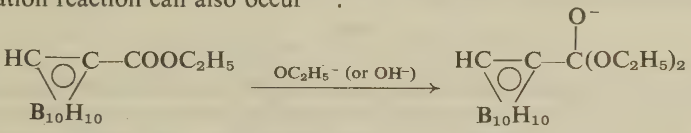
$$HC{\vdots}C.C_6H_5 + B_{10}H_{13}Cl \rightarrow 8\text{-}B_{10}H_9ClC_2H.C_6H_5 + 2H_2 \quad (314\text{–}15)$$

The side chains of alkenyl carboranes may be oxidized by potassium permanganate or hydrogenated, but they show little reactivity towards electrophilic reagents. Bromine adds to a side chain, such as $\text{—}(CH_2)_2\text{—}CH{=}CH_2$ but not to short or substituted systems such as $\text{—}CH{=}CH_2$ or $\text{—}CH{=}CHCH_3$. Perfluoroacetic acid converts these side chains to epoxides.[186, 240] The epoxides may be converted to diols by oxidation with refluxing dilute sulphuric acid.[240] Two distinct isomers of $B_{10}H_{10}C_2H.CH_2CHOH.CH_2OH$ have been obtained.[240]

Alcohol and carboxylic acid derivatives are not usually obtained by the direct route, owing to competitive reactions with decaborane itself. The monocarboxylic acids may be converted to acid chlorides, amides and esters by standard methods, but the dicarboxylic acids are much less reactive.[186, 240, 316] However, $B_{10}H_{10}C_2(CH_2COOH)_2$, which is obtained by oxidation of $B_{10}H_{10}C_2(CH_2CH_2OH)_2$ with chromic acid, undergoes the reactions usually associated with a dicarboxylic acid[240, 257]:



Carborane-carboxylic esters are not easily saponified, since a competing decarboxylation reaction can also occur[277]:



$$\longrightarrow B_{10}H_{10}C_2H^- + (C_2H_5O)_2CO \xrightarrow{H^+} 1{:}2\text{-}C_2B_{10}H_{12}$$

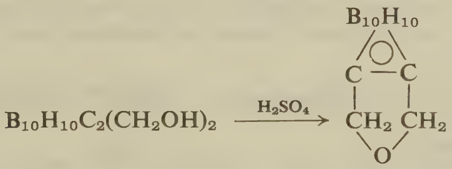
The C—C bonds of some carboranyl ketones and alcohols have also been cleaved by sodium ethoxide[278–9], ethyl sodium or sodamide.[317] Other cleavage reactions are shown below[186, 277]:

$$B_{10}H_{10}C_2H[CON(C_2H_5)_2] \xrightarrow{LiAlH_4} 1{:}2\text{-}C_2B_{10}H_{12} + (C_2H_5)_2NH$$

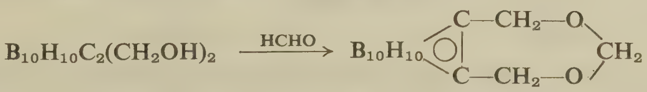
$$B_{10}H_{10}C_2(CH_2OH)_2 \xrightarrow[OH^-]{KMnO_4} 1{:}2\text{-}C_2B_{10}H_{12}$$

Hydroxyalkylcarboranes undergo elimination reactions at high temperatures or in the presence of hot, concentrated sulphuric acid[240]:

$$(B_{10}H_{10}C_2H)_2CHOOCCH_3 \xrightarrow{500°C} B_{10}H_{10}C_2H\text{—}CH_2.CH{:}CH.C_2HB_{10}H_{10}$$



Such carbon exocyclic compounds are readily formed.[318] The same dihydric alcohol gives a cyclic poly formal with formaldehyde[319]:



Nevertheless, the general chemistry does closely parallel that of conventional organic systems. Grignard and organo-lithium compounds have been widely used in synthetic work (see below). In addition, other standard organic reactions have been used for the preparation of hydrocarbon and *C*-halogen derivatives[174, 287, 320–5], ethers and epoxides[31, 186, 240, 322, 326–7], alcohols and diols[9, 199, 214, 240, 257, 286, 288, 309, 317, 326–30], aldehydes and ketones[286, 322, 328–38], carboxylic acids and their derivatives[174, 240, 257, 286, 310, 312, 322, 327–8, 334–5, 339–41], esters[240, 321, 331, 334, 342–3], and amines and other nitrogen derivatives.[9, 174, 240, 262, 286, 309–10, 322, 324, 327, 332, 338, 343–6] A detailed list of the compounds prepared by such standard methods may be obtained from Table XXVIII.

Metal (Li, Mg, Zn, Hg) *Derivatives*

Organo-lithium compounds are widely used in synthetic reactions. They are prepared by the reaction of *n*-butyllithium or phenyllithium on 1:2-$C_2B_{10}H_{12}$ or $B_{10}H_{10}C_2HR$[186, 206, 240, 347]:

$$B_{10}H_{10}C_2HR \xrightarrow[\text{benzene at } 70^\circ C]{LiC_4H_9} B_{10}H_{10}C_2RLi$$

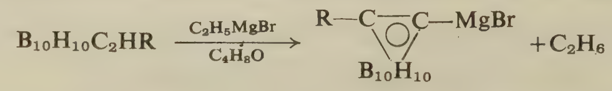
To obtain $B_{10}H_{10}C_2HLi$, the reaction must be carried out in ether at 0°C using an excess of 1:2-$C_2B_{10}H_{12}$.[240] This compound and its Grignard analogue tend to disproportionate partially[348]:

$$\underset{(80\%)}{2B_{10}H_{10}C_2HLi} \rightleftharpoons \underset{(10\%)}{B_{10}H_{10}C_2H_2} + \underset{(10\%)}{B_{10}H_{10}C_2Li_2}$$

Such disproportionation is less marked for the monolithium derivative of 1:7-$C_2B_{10}H_{12}$. $B_{10}H_{10}C_2Li_2$ is obtained by the use of excess of butyllithium. Sodium, lithium, potassium and calcium derivatives can be obtained by reaction with metal amides in liquid ammonia[316, 349–51]:

$$B_{10}H_{10}C_2RH \xrightarrow{MNH_2} B_{10}H_{10}C_2RM$$

Evidently the hydrogen atoms which are bonded to the two carbon atoms are distinctly acidic, owing to the strongly electron-withdrawing nucleus. If this electron-withdrawing power is increased by halogen substitution, the acidity becomes more marked. Thus $B_{10}Cl_{10}C_2H_2$ is a true protonic acid, soluble in sodium hydroxide.[352] There have been several studies of the use of Grignard reactions in syntheses.[186, 199, 240, 321, 329, 348, 353–4] Ethyl magnesium bromide reacts smoothly with 1:2-$C_2B_{10}H_{12}$, 1:7-$C_2B_{10}H_{12}$ and $B_{10}H_{10}C_2HCH_3$ in tetrahydrofuran[186, 355]:

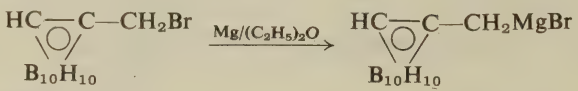


$$B_{10}H_{10}C_2HR \xrightarrow[C_4H_8O]{C_2H_5MgBr} \underset{B_{10}H_{10}}{R{-}C{-}C{-}MgBr} + C_2H_6$$

A Frankland reagent has been similarly prepared in hexamethyltriamidophosphate[356]:

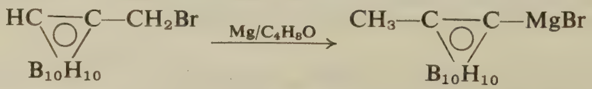
$$2B_{10}H_{10}C_2H.C_6H_5 + Zn(C_2H_5)_2 \rightarrow (B_{10}H_{10}C_2.C_6H_5)_2Zn + 2C_2H_6$$

An extraordinary reaction has been observed during attempts to prepare a halogeno-alkyl side-chain Grignard reagent in tetrahydrofuran.[186, 248] In ether the reaction proceeds:



$$\underset{B_{10}H_{10}}{HC{-}C{-}CH_2Br} \xrightarrow{Mg/(C_2H_5)_2O} \underset{B_{10}H_{10}}{HC{-}C{-}CH_2MgBr}$$

but in tetrahydrofuran:



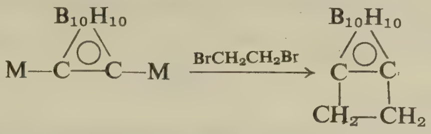
$$\underset{B_{10}H_{10}}{HC{-}C{-}CH_2Br} \xrightarrow{Mg/C_4H_8O} \underset{B_{10}H_{10}}{CH_3{-}C{-}C{-}MgBr}$$

The two isomeric acids, $B_{10}H_{10}C_2H(CH_2COOH)$ and $B_{10}H_{10}C_2CH_3(COOH)$, were obtained on reaction of the Grignard reagents with carbon dioxide. These isomerization reactions of Grignard reagents have been studied in more detail.[353, 357] The chloroalkyl compound undergoes rearrangement, even in ether. An early report of the inertness of Grignard reagents[240] has been shown to be incorrect[348, 354, 358–9] and they are very useful in synthesis.[7, 199]

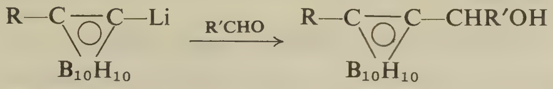
The Group I metal reagents and Grignard reagents have been used to synthesize many alkyl and aryl derivatives of 1:2-$C_2B_{10}H_{12}$ and 1:7-$C_2B_{10}H_{12}$. The typical reactions below illustrate the general synthetic value of these reagents[360–1]:

$$B_{10}H_{10}C_2RM + R'X \rightarrow B_{10}H_{10}C_2RR'$$
$$B_{10}Cl_{10}C_2RM + R'X \rightarrow B_{10}Cl_{10}C_2RR'$$

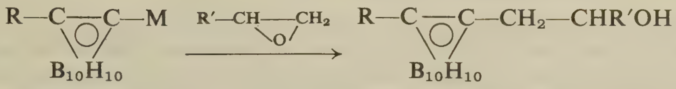
Numerous other preparations of alkyl and aryl derivatives from such reagents have been described.[14,186,199,240,287,290,309,322–3,350–1,353,362–5] Exocyclic rings have been generated[362,366–7],



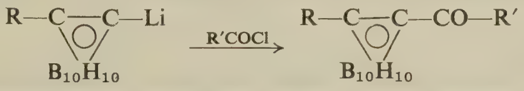
as have side-chain alcohols[240,340,349–50,368],



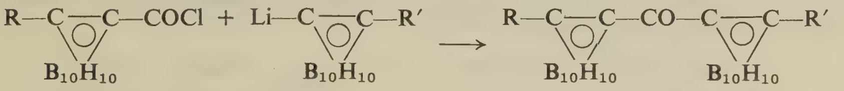
and[186,240,335]



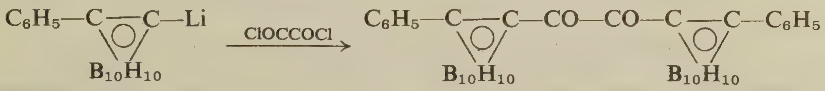
Many other similar preparations of alcohols have been described[14,201,322,328,331,341,369–71] and ketones have been made from acid chlorides[317,328,337,340–1,354,369,371], e.g. simple carboxylic acid chlorides[371–2]:



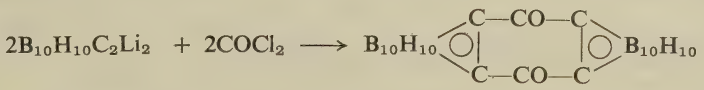
or carborane-substituted acid chlorides[371],



dicarboxylic acid chlorides[371],



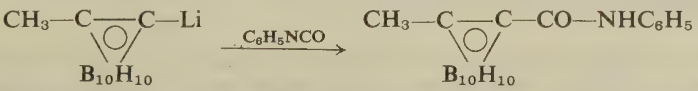
or phosgene[373],



Metal reagents have been used to prepare other difunctional compounds.[200,257,328–9,335,340–1,362] A large number of carboxylic acids have been similarly prepared[81,186,240,248,338–9,341–2,367,375–7], for example[347],

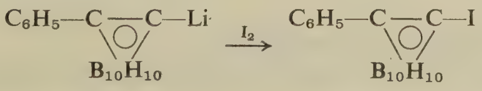
$$B_{10}H_{10}C_2R.MgBr + CO_2 \rightarrow B_{10}H_{10}C_2R(COOH)$$

Substituted acid amides can be synthesized from isocyanates[351,371]:



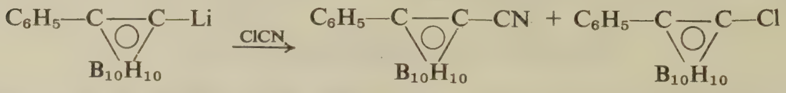
and a similar reaction occurs with phenyl isothiocyanate.

C-Halogeno compounds[332,335,349–50,358–9,374,379–80] are readily prepared, e.g.[186,360,373,378],



In methods analogous to purely organic procedures, nitrogen-containing side chains can easily be inserted[174, 332, 381]:

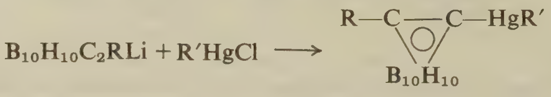
$$B_{10}H_{10}C_2HLi \xrightarrow{NOCl} B_{10}H_{10}C_2H.NO$$



$$C_6H_5—C(B_{10}H_{10})C—Li \xrightarrow{ClCN} C_6H_5—C(B_{10}H_{10})C—CN + C_6H_5—C(B_{10}H_{10})C—Cl$$

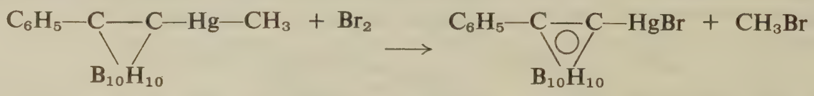
Mercury derivatives can be prepared by the reaction of the lithium or magnesium derivatives with mercuric chlorides, alkyl mercuric chlorides or their aryl analogues[6, 332, 379, 382–8]:

$$2B_{10}H_{10}C_2RLi + HgCl_2 \rightarrow Hg(C_2RB_{10}H_{10})_2$$



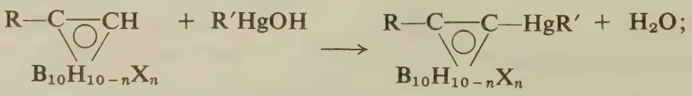
$$B_{10}H_{10}C_2RLi + R'HgCl \longrightarrow R—C(B_{10}H_{10})C—HgR'$$

No traces of $B_{10}H_{10}C_2R.HgCl$ derivatives are obtained. This is due to the rapid alkylation of the second halogen atom rather than to the disproportionation of these compounds.[7] The carboranyl-mercuric halides may be prepared by treating the corresponding alkyl compounds with halogens[384]:



$$C_6H_5—C(B_{10}H_{10})C—Hg—CH_3 + Br_2 \longrightarrow C_6H_5—C(B_{10}H_{10})C—HgBr + CH_3Br$$

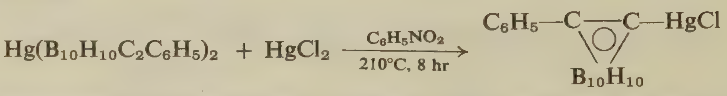
The ^{81}Br nuclear-quadrapole-resonance spectra of these compounds[7] indicate that the mercury-bromine bond is more covalent in carboranyl compounds than in mercuric bromide. Alkyl derivatives of $1:2\text{-}C_2B_{10}H_{12}$ undergo direct *C*-mercuration with organo-mercuric hydroxides[389]:



$$R—C(B_{10}H_{10-n}X_n)CH + R'HgOH \longrightarrow R—C(B_{10}H_{10-n}X_n)C—HgR' + H_2O;$$

$R = H, CH_3, C_6H_5;\ R' = CH_3, C_6H_5;\ X = Cl, Br;\ n = 0, 2, 4$

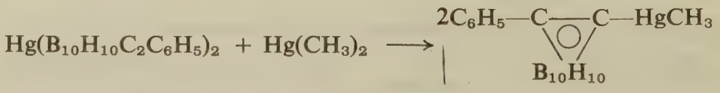
Carbon-mercury bonds are not easily split by hydrochloric acid or mercuric chloride[332, 384]:



$$Hg(B_{10}H_{10}C_2C_6H_5)_2 + HgCl_2 \xrightarrow[210°C,\ 8\ hr]{C_6H_5NO_2} C_6H_5—C(B_{10}H_{10})C—HgCl$$

Carboranyl mercuric halides are not made symmetrical by potassium cyanide or iodide.

Bis(phenyl-1:2-dicarbadodecaboranyl)mercury reacts under severe conditions with dimethylmercury[6]:



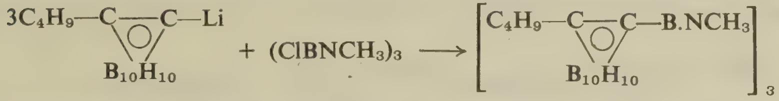
$$Hg(B_{10}H_{10}C_2C_6H_5)_2 + Hg(CH_3)_2 \longrightarrow 2C_6H_5—C(B_{10}H_{10})C—HgCH_3$$

Mercury-carboranyl bonds are readily cleaved in inert solvents by *n*-butyllithium and lithium aluminium hydride, but not by lithium itself. The mercury derivatives of $1:2\text{-}C_2B_{10}H_{12}$ form complexes with 2:2′-bipyridyl and *o*-phenanthroline.[6, 390] The polarographic reduction of carboranyl-mercury compounds has been investigated.[384, 391]

Non-metal (B, Si, Ge, Sn, P, S) *Derivatives*

Boron derivatives of $1:2\text{-}C_2B_{10}H_{12}$ were obtained by the reaction of lithium derivatives with bisdimethylaminochloroborane(3) and the methylaminochloroborane trimer $(ClBNCH_3)_3$[392]:

$$B_{10}H_{10}C_2HLi + ClB[N(CH_3)_2]_2 \xrightarrow{0°C} B_{10}H_{10}C_2H.B[N(CH_3)_2]_2$$

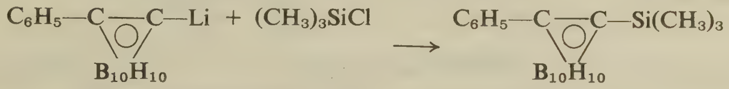


Carborane derivatives have been obtained[118] by treating $1{:}2\text{-}C_2B_{10}H_{12}$ and its *C*-methyl derivative with $2{:}3\text{-}C_2B_9H_{11}$ in the presence of *n*-butyllithium:

$$B_{10}H_{10}C_2H.CH_3 \xrightarrow[LiC_4H_9]{C_2B_9H_{11}} 4\text{-}(B_{10}H_{10}C_2CH_3)\text{-}1{:}7\text{-}C_2B_9H_{11}^-$$

This ion was isolated as its tetramethylammonium salt. On treatment with polyphosphoric acid, the neutral molecule $4\text{-}(B_{10}H_{10}C_2CH_3)\text{-}2{:}3\text{-}C_2B_9H_{10}$ was obtained (Fig. 35).

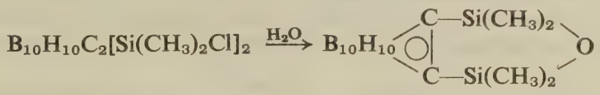
Numerous silicon derivatives have been synthesized by similar reactions[240, 258–9, 353, 379, 382–3, 393–6]:

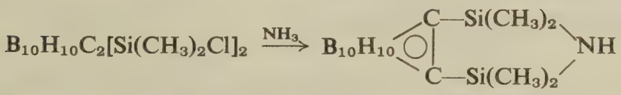


$$2B_{10}H_{10}C_2HLi + (CH_3)_2SiCl_2 \rightarrow (CH_3)_2Si(C_2HB_{10}H_{10})_2$$

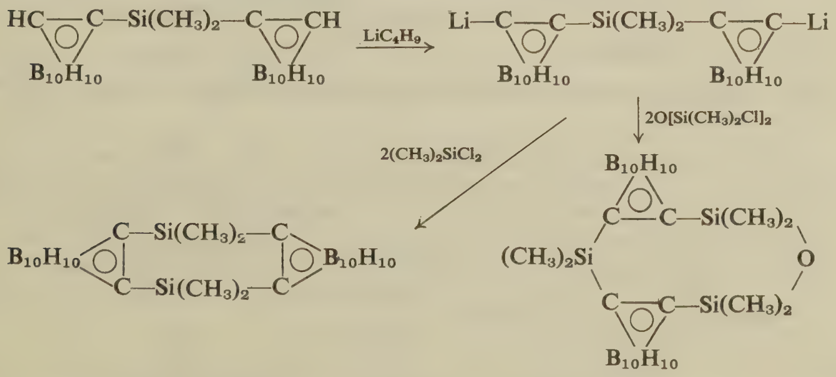
$$B_{10}H_{10}C_2Li_2 + SiCl_4 \rightarrow B_{10}H_{10}C_2(SiCl_3)_2$$

Hydrolysis or ammonolysis of the corresponding bis(chlorodimethylsilyl)-derivative leads to the formation of exocyclic silicon compounds[258]:

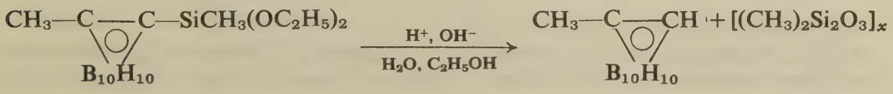




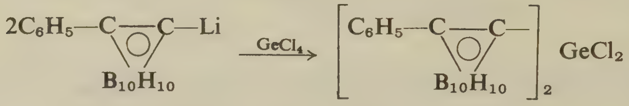
The versatile synthetic possibilities are demonstrated by the set of reactions[259]:

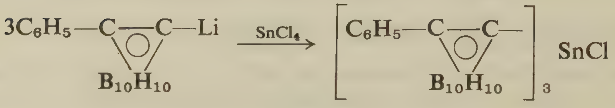


The strongly electron-withdrawing carborane nucleus makes the silicon-halogen bonds difficult to hydrolyze, but conversely the silicon–carbon bonds can be cleaved by bases[258, 353]:



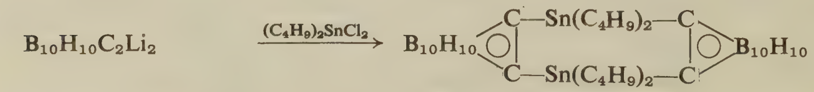
Silane derivatives of 1:2-$C_2B_{10}H_{12}$ can be isomerized to the corresponding 1:7-$C_2B_{10}H_{12}$ derivatives at 260–300°C.[397] Corresponding germanium and tin compounds can be obtained by similar reactions.[181, 379, 382–3, 398] In contrast to silicon and germanium, tin atoms can accommodate three icosahedral carborane groups.





$$B_{10}H_{10}C_2HLi \xrightarrow{(C_6H_5)_3SnCl} B_{10}H_{10}C_2H.Sn(C_6H_5)_3$$

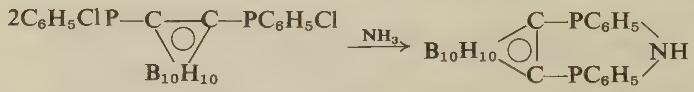
$$B_{10}H_{10}C_2Li_2 \xrightarrow{(C_6H_5)_3SnCl} B_{10}H_{10}C_2[Sn(C_6H_5)_3]_2$$

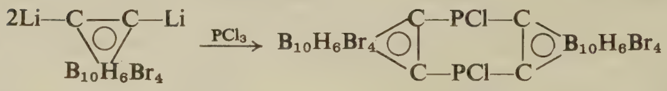


The Sn—Cl and Sn—C bonds in these compounds are attacked by bases at a similar rate.[181] The comparable polarity of the Sn—Cl and Sn—C bonds has been demonstrated in a Mössbauer effect study.[399]

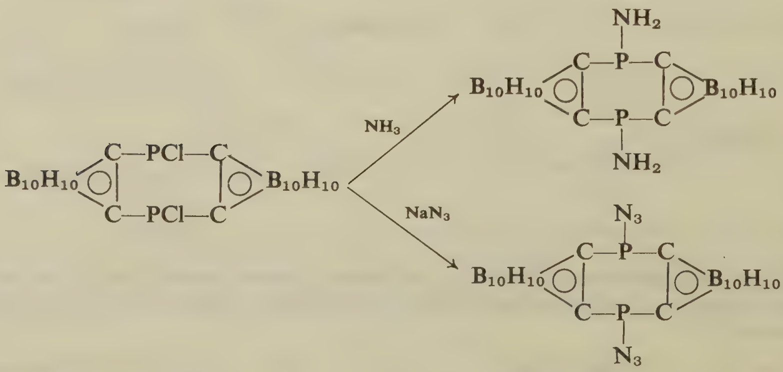
Phosphorus derivatives of 1:2-$C_2B_{10}H_{12}$ and its *B*-halogen derivatives have been obtained by similar methods.[260, 363, 379, 382–3, 400–4]

$$B_{10}H_{10}C_2Li_2 \xrightarrow{(C_6H_5)_2PCl} B_{10}H_{10}C_2[P(C_6H_5)_2]_2$$



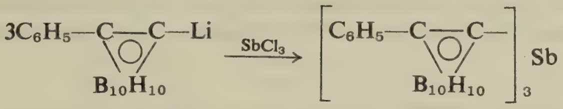


The cyclic chlorophospha-compound reacts with ammonia and sodium azide[260]:



The azidophospha-compound reacts with triphenylphosphine to give a stable phosphine-imino compound[260], and a polymeric binder has been obtained with

$(C_6H_5)_2P.C_6H_4.P(C_6H_5)_2$.[363] The bis(diphenylphosphino)-derivatives of 1:2-$C_2B_{10}H_{12}$ form complexes with metal halides and carbonyls.[402, 405–7] Similar arsenic and antimony compounds and complexes have been prepared.[290, 408] Only two of the chlorine atoms of phosphorus trichloride can be replaced by an icosahedral carboranyl group, whereas all three chlorine atoms of arsenic and antimony chlorides can be so replaced[388]:



Sulphur derivatives are obtained by similar methods[341, 379, 409–11]:

$$B_{10}H_{10}C_2Li_2 + RSSR \longrightarrow B_{10}H_{10}C_2(SR)_2$$

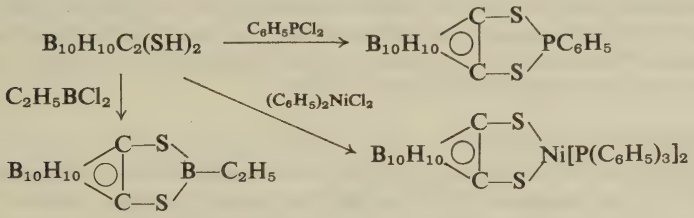
$$B_{10}H_{10}C_2Li_2 + 2S \xrightarrow{H_2O} B_{10}H_{10}C_2(SH)_2$$

The C—S bond is cleaved by *n*-butyllithium[409]:

$$B_{10}H_{10}C_2(SCH_3)_2 \xrightarrow[(C_2H_5)_2O]{2LiC_4H_9} B_{10}H_{10}C_2Li_2 + 2C_4H_9SCH_3$$

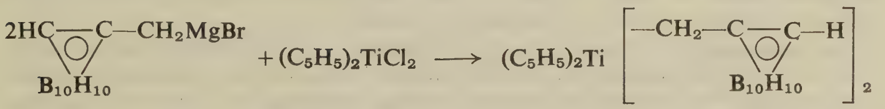
$B_{10}H_{10}C_2(SH)_2$ readily forms a wide range of exocyclic derivatives and complexes[407, 409–10, 412–13]:

$$B_{10}H_{10}C_2(SH)_2 + Cl_2 \rightarrow B_{10}H_{10}C_2(SCl)_2$$

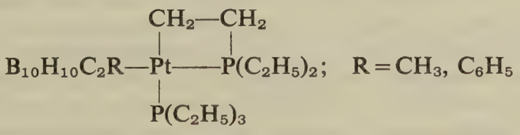


Derivatives Containing Titanium, Iron and Platinum

$B_{10}H_{10}C_2H(CH_2MgBr)$ reacts with bis(*cyclo*pentadienyl)titanium dichloride to give a σ-bonded titanium derivative[385]:



The σ-bonded iron compound, $B_{10}H_{10}C_2CH_3.Fe(CO)_2C_5H_5$, has also been obtained.[128] The 1:2- and 1:7-dicarbadodecaborane compounds of the general formula $B_{10}H_{10}C_2RLi$ are reported to react with *trans*-$PtCl_2[P(C_2H_5)_3]_2$ to give monomeric diamagnetic products of apparent formula $B_{10}H_{10}C_2R.Pt[P(C_2H_5)_3]_2$. It was suggested that one hydrogen atom of one of the ethyl groups might have been liberated to give the four-co-ordinate species:



$$\begin{array}{l} \qquad\qquad\qquad CH_2\text{—}CH_2 \\ B_{10}H_{10}C_2R\text{—}Pt\text{——}P(C_2H_5)_2; \quad R = CH_3, C_6H_5 \\ \qquad\qquad\qquad P(C_2H_5)_3 \end{array}$$

Evidently this system merits further investigation.

A number of *C*-substituted derivatives of 1:2-$C_2B_{10}H_{12}$ have been the subject of physico-chemical investigations. There have been *X*-ray investigations of the structures of $B_{10}H_{10}C_2(CH_2Br)_2$[245–7], $B_{10}H_{10}C_2C_6H_5.HgBr$, $B_{10}H_{10}C_2C_6H_5.HgCH_3$

and $Hg(B_{10}H_{10}C_2C_6H_5)_2$[254], and $B_{10}H_{10}C_2H—C_2HB_{10}H_{10}$[254], as well as an electron-diffraction study of $B_{10}H_{10}C_2(CH_3)_2$ which have established the structure unambiguously.[256] The Mössbauer spectrum of the iron tricarbonyl complex of $B_{10}H_{10}C_2[As(CH_3)_2]_2$ has been reported[408], as have the spectra of some tin derivatives.[399] ^{19}F nuclear-magnetic-resonance spectra of some fluorinated derivatives have been studied[281, 310], as have the ^{35}Cl and ^{79}Br nuclear-quadrapole-resonance spectra of some chlorine and bromine analogues.[415–16] There have also been detailed i.r. studies of many derivatives.[282–3] The following dipole moments have been recorded[291, 294]:

Table XXVIIIa.—Dipole Moments of Derivatives of Closo-1:2-*dicarbadodecaborane*(12)

Formula	$C\,m \times 10^{-30}$	D
$B_{10}H_{10}C_2H.CH_3$	15·8	4·75
$B_{10}H_{10}C_2Br_2$	9·4	2·82
$B_{10}H_{10}C_2CH_3Br$	12·4–12·6	3·72–3·78
$B_{10}H_{10}C_2HBr$	11·0–11·5	3·31–3·45
$B_{10}H_{10}C_2HCl$	10·3	3·10
$B_{10}H_{10}C_2CH_3Cl$	11·9–12·2	3·57–3·65

The polarographic reduction of some 1:2-dicarbadodecaboranyl ketones to alcohols has been investigated[337], and the rate of isomerization of $B_{10}H_{10}C_2(SiR_3)_2$ compounds and their analogues to the corresponding 1:7-compounds when heated has been studied.[397] Dissociation constants of carboxylic acids and amines are recorded in appropriate sections of Table XXVIII.

BORON-SUBSTITUTED DERIVATIVES

Halogenation of 1:2-$C_2B_{10}H_{12}$ with gaseous halogens occurs in a stepwise fashion, which can be moderated by adjusting the solvent, reaction time or temperature, or by the use of u.-v. radiation or a Friedel–Crafts catalyst. Alternative halogenating reagents are metal polyhalides[417] or an aqueous mixture of $X_2 + XO_3^-$; $X = Br, I$.[418] The ten boron atoms of the substrate offer possibilities for the formation of numerous isomers, and there are many uncertain data in the literature which require collation. In view of these doubts, a number of 'compounds' recorded in Table XXVIII may prove to be mixtures of isomers.

The compounds $B_{10}H_8Cl_2C_2H_2$ (two isomers), $B_{10}H_7Cl_3C_2H_2$, $B_{10}H_6Cl_4C_2H_2$ (two isomers), $B_{10}H_4Cl_6C_2H_2$, $B_{10}H_2Cl_8C_2H_2$, $B_{10}Cl_{10}C_2H_2$ and $B_{10}Cl_{10}C_2HCl$ were reported[185, 419] to be the products of direct chlorination of *closo*-1:2-dicarbadodecaborane(12). Infra-red and ^{11}B n.m.r. spectral studies provided ample evidence of preferential boron-substitution by chlorine, which is an electrophilic reagent. The perchloro-compound, $C_2B_{10}Cl_{12}$, was obtained only by using *N*-chlorosuccinamide.[360] *X*-Ray studies of $B_{10}H_2Cl_8C_2H_2$ indicated that the boron atoms normally numbered 3 and 6 as in Fig. 12 are unsubstituted.[243–4] These two atoms, adjacent to the two carbon atoms, are those predicted to be the least negatively charged. Careful and extensive studies[420–3] have indeed established that the most electro-negative atoms, i.e. B^9 and B^{12}, are substituted first, followed by atoms B^8 and B^{10}. The situation among tetrahalogen and octahalogen derivatives has not been closely investigated. When the carbon atoms themselves are asymmetrically substituted, the number of possible isomers is doubled, and in general such pairs of isomers can be obtained experimentally. Isomer ratios have been studied in detail[424], as have the rearrangements of halogen derivatives of 1:2-$C_2B_{10}H_{12}$.[425–6] Results from bromination are similar.[427] *X*-Ray studies of 9-$B_{10}H_9BrC_2H_2$, 9:12-$B_{10}H_8Br_2C_2H_2$, 8:9:12-$B_{10}H_7Br_3C_2H_2$ and 8:9:10:12-$B_{10}H_6Br_4C_2(CH_3)_2$ have established that the boron atoms are indeed subject to electrophilic halogenation in the following order:

$B^9 = B^{12} > B^8 = B^{10} >$ others.[249–52] The B—Cl bonds do not undergo exchange with trifluorodichloroantimony(V) nor do they react with ammonia or amines.[185] The chlorine atoms are removed by boiling with alcoholic hydrogen peroxide but B—F bonds in fluorinated analogues are smoothly hydrolyzed by water.[428] $B_{10}Cl_{10}C_2H_2$ and $B_{10}Cl_{10}C_2HCl$ can be titrated in ethanol or aqueous ethanol as diprotic and monoprotic acids respectively. They form triethylammonium salts with triethylamine.[185] Alkyl and aryl substituents on the carbon atoms are often halogenated themselves, following halogenation of boron atoms B^8, B^9, B^{10} and B^{12}. $B_{10}H_6Cl_4C_2H.C_6Cl_5$ and $B_{10}H_6Br_4C_2H.C_6H_2Br_3$ have been obtained in this way from $B_{10}H_{10}C_2H.C_6H_5$.[292, 429–30] All ten boron atoms of 1:2-, 1:7- and 1:12-$C_2B_{10}H_{12}$ have been fluorinated by direct reaction with fluorine in liquid hydrogen fluoride.[428, 431]

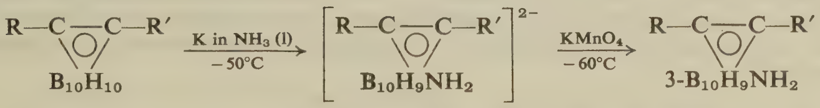
Halogen atoms have been introduced preferentially, but not exclusively, into the 8-position by direct synthesis from acetylenes and halogenodecaboranes[314–15]:

$$B_{10}H_{13}Br + C_6H_5.C{:}CH \xrightarrow{CH_3CN} 8\text{-}B_{10}H_9BrC_2H.C_6H_5$$

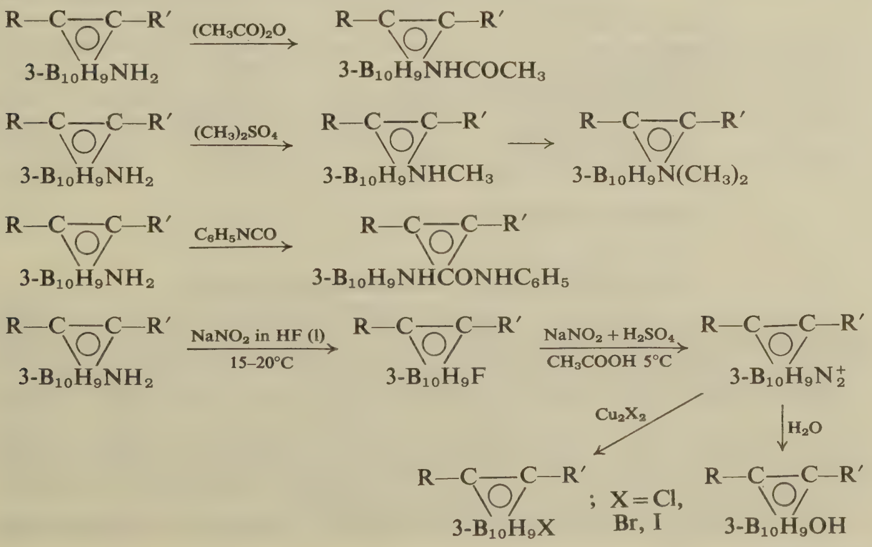
Two methods have been devised for the introduction of substituents preferentially into the 3-position of 1:2-$C_2B_{10}H_{12}$. Firstly, the C_2B_{10} icosahedron can be reconstructed from (3):1:2-$C_2B_9H_{11}^{2-}$ by reaction with phenyldichloroborane(3) or ethyldichloroborane(3)[433–4]:

$$Na_2C_2B_9H_{11} + C_6H_5BCl_2 \rightarrow 3\text{-}B_{10}H_9C_6H_5C_2H_2 + 2NaCl$$

A similar reaction has been observed with diethylaminodichloroborane(3).[435] The 3-substituted compounds could be reconverted to 6-substituted derivatives of the (3):1:2-$C_2B_9H_{11}^{2-}$ ion, so that further reaction with phenyldichloroborane(3) or ethyldichloroborane(3) can lead to 3:6-disubstituted derivatives of 1:2-$C_2B_{10}H_{12}$. Secondly, an amino group can be inserted into the 3-position by the following procedure[436–7]:



A similar product was obtained using piperidine instead of ammonia. The 3-amino group shows characteristics of both aliphatic and aromatic amines; it forms salts with acids and may be alkylated, acylated or diazotized. The versatile synthetic possibilities are illustrated by the following reactions:



3-$B_{10}H_9.CHO.C_2H_2$ and 3-$B_{10}H_9.COOH.C_2H_2$ have been synthesized from 3-vinyl-1:2-dicarbadodecaborane.[438] Nitration of 1:2-$C_2B_{10}H_{12}$ causes reaction at the 9-position, but only the 9-hydroxy- and 9-nitrato-derivatives can be isolated.[274, 439–40] The phenol can be esterified. A number of poorly characterized *B*-alkyl derivatives of 1:2-$C_2B_{10}H_{12}$, only tentatively assigned from mass-spectral evidence, are mentioned in industrial research reports.[9] The iodine atom in 9-$B_{10}H_9IC_2H_2$ undergoes exchange with ^{131}I in tetrahydrofuran.[441] Following the recognition that this B—I bond is reactive, an attempted Ullmann reaction[442] led to the formation of 9:9′-bis(1:2-dicarbadodecaboranyl)[442]:

$$9\text{-}B_{10}H_9IC_2H_2 \xrightarrow{Cu + C_4H_8O} 9{:}9'\text{-}\left[\begin{array}{l} B_{10}H_9C_2H_2 \\ | \\ B_{10}H_9C_2H_2 \end{array}\right]$$

The reader should note that this reference and other papers by these workers[422] unaccountably employ a numbering system for the boron atoms which differs from that used by most other workers. This arises from the selection of a different atom in the lower pentagon as B^7 so that the boron atoms B^{7-11} of the more commonly used designation correspond to boron atoms B^{8-11} and B^7 of these papers.

A number of amine, dimethyl sulphoxide, dimethylformamide and dioxan complexes of halogen derivatives of 1:2-$C_2B_{10}H_{12}$ have been described.[185–6, 443–4] Other authors have described the preparation of derivatives which are substituted on the boron atoms with halogens and on the carbon atoms with alkyl, aryl and organo-mercury, -silicon, -phosphorus and -sulphur groups.[445–9] A complete list can be obtained from Table XXVIII. When the compound is heated, a halogen atom substituted on one of the carbon atoms migrates to one of the boron atoms B^8, B^9, B^{10} or B^{12}.

Among published physico-chemical investigations of these compounds are *X*-ray investigations of 12-$B_{10}H_9IC_2HC_6H_5$[253], and the bromo-derivatives mentioned above.[249] There has been a ^{35}Cl nuclear-quadrupole-resonance study of a number of *C*- and *B*-chloro-derivatives.[416, 450] The following dipole moments have been recorded[291, 293–4, 451]:

Table XXVIIIb.—Dipole Moments of B-halogenated Derivatives of Closo-1:2-*dicarbadodecaborane*(12)

Formula	C m × 10^{-30}	D
9-$B_{10}H_9ClC_2H_2$	19·8	5·93
$B_{10}Cl_{10}C_2H_2$	21·2	6·36
9:12-$B_{10}H_8Cl_2C_2H_2$	23·3	6·98
$B_{10}H_9ClC_2CH_3Cl$	12·4–12·6	3·72–3·78
9:12-$B_{10}H_8Br_2C_2H_2$	23·9–24·0	7·18–7·21
9-$B_{10}H_9IC_2HC_6H_5$	19·7	5·96
9:12-$B_{10}H_8I_2C_2HC_6H_5$	23·4	7·02

Derivatives of *Closo*-1:7-dicarbadodecaborane(12)

The general chemistry of 1:7-$C_2B_{10}H_{12}$ closely parallels that of the 1:2-isomer. Differences may be mainly associated with the lower electron-withdrawing power of the nucleus manifested, for example, in the inability to form small exocyclic *C*-substituted compounds; instead, polymeric products are more easily obtained. Derivatives of 1:7-$C_2B_{10}H_{12}$ are listed in Table XXXIX. The principal methods of preparation correspond to those used for the 1:2-isomers, but direct synthesis from acetylenes is not possible. Alternatively, some compounds have been prepared by heating the corresponding 1:2-$C_2B_{10}H_{12}$ derivative.

The conventional shorthand formula for *closo*-1:7-dimethyl-1:7-dicarbadodecaborane(12) is $CH_3.CB_{10}H_{10}C.CH_3$—the form used in this account. It has been customary to prepare a few derivatives of this isomer together with the derivatives of the 1:2-isomer for comparative studies. In addition there are specific references to the corresponding derivatives of the 1:7-isomer.[452-3] $HOOC.CB_{10}H_{10}C.COOH$ may be esterified more easily than $B_{10}H_{10}C_2(COOH)_2$, but the C—C bonds of $HOCH_2.CB_{10}H_{10}C.CH_2OH$ are split by alkaline potassium permanganate.[81] Organo-element derivatives are readily obtained from the lithium derivatives or Grignard reagents[386]:

$$CH_3.CB_{10}H_{10}C.Li \xrightarrow{RHgCl} CH_3.CB_{10}H_{10}C.HgR$$

A number of other mercury derivatives have been prepared by similar reactions.[389-90, 409]

$$Li.CB_{10}H_{10}C.Li \xrightarrow{RSSR} RS.CB_{10}H_{10}C.SR$$

Other sulphur derivatives have been similarly prepared.[371, 393, 412, 454]

$$Li.CB_{10}H_{10}C.Li \xrightarrow{CH_3SiCl_3} CH_3Cl_2Si.CB_{10}H_{10}C.SiCH_3Cl_2$$

A number of similar methods are available for the preparation of other silicon derivatives.[282, 394, 397-8, 414, 455-6]

$$Li.CB_{10}H_{10}C.Li \xrightarrow{GeCl_4} Cl_3Ge.CB_{10}H_{10}C.GeCl_3$$

$$Li.CB_{10}H_{10}C.Li \xrightarrow{(C_6H_5)_2PCl} (C_6H_5)_2P.CB_{10}H_{10}C.P(C_6H_5)_2$$

$$CH_3.CB_{10}H_{10}C.Li \xrightarrow{Pt[P(C_2H_5)_3]_2Cl_2} CH_3.CB_{10}H_{10}C.Pt[P(C_2H_5)_3]_2$$

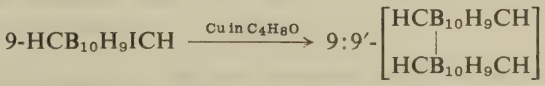
(see the discussion of loss of a hydrogen atom in the 1:2-isomer of this compound on p. 481 above).

On the other hand, reactions of the dilithio-compound with diaryl- and dialkyl-germanium or tin chlorides produce mainly polymeric products[398, 412, 457-9]:

$$Li.CB_{10}H_{10}C.Li \xrightarrow{(C_6H_5)_2GeCl_2} (C_6H_5)_2ClGe\text{-}[—CB_{10}H_{10}C—Ge(C_6H_5)_2—]_n\text{-}Cl$$

Direct *C*-mercuration of 1:7-$C_2B_{10}H_{12}$ by organo-mercuric hydroxides does not occur under conditions similar to those used for 1:2-$C_2B_{10}H_{12}$.[389] Organo-mercuric derivatives of 1:7-$C_2B_{10}H_{12}$ are more reactive towards electrophilic reagents than their 1:2-counterparts.[386]

The boron atoms in positions 9 and 10 (Fig. 13) are those most subject to electrophilic halogenation[420-2, 460], followed by those at the 5- and 12-positions. All four isomers, 2-, 4-, 5- and 9-H—$CB_{10}H_9X$C—H, have been described for X = F, Cl and Br.[461] The preparations of a large number of *B*-halogenated derivatives have been described (Table XXIX).[9, 241, 304, 360, 363, 391, 418, 428-9, 431, 441, 444, 447, 449, 451, 456, 461-6] The biscarboranyl compound 9:9′-$(HCB_{10}H_9CH)_2$ has been prepared by an Ullmann reaction.[442]



$$9\text{-}HCB_{10}H_9ICH \xrightarrow{Cu\ in\ C_4H_8O} 9{:}9'\text{-}\left[\begin{array}{c}HCB_{10}H_9CH\\ |\\ HCB_{10}H_9CH\end{array}\right]$$

However, it has not yet been proved possible to introduce an amino-group at a boron atom[436-7], because when $R.CB_{10}H_{10}C.R'$ compounds are treated with alkali metals in liquid ammonia, they rearrange to the corresponding 1:2-compounds.[268] A similar isomerization occurs with the sodium derivative of naphthalene.[267]

Among physico-chemical studies, there have been *X*-ray investigations of $HCB_{10}Cl_{10}CH$[271], 9:10-$HCB_{10}H_8Br_2CH$[272], and 9-$HCB_{10}H_9ICH$.[273] ^{35}Cl nuclear-quadrupole-resonance and ^{19}F nuclear-magnetic-resonance spectra[281, 310] have been studied in detail for suitable derivatives. The polarographic reduction of some

C-ketone and *C*-mercury derivatives has been investigated.[337, 391] The following dipole moments have been reported[291, 293, 451]:

Table XXIXa.—Dipole Moments of Derivatives of Closo-1:7-*dicarbadodecaborane*(12)

Formula	C m × 10^{-30}	D
$BrCB_{10}H_{10}CBr$	5·47	1·64
$HCB_{10}Cl_{10}CH$	14·6	4·39
9-$HCB_{10}H_9ClCH$	14·1	4·22
9:10-$HCB_{10}H_8Cl_2CH$	17·9	5·37
$HCB_{10}H_7Cl_3CH$	19·5	5·86
$HCB_{10}H_6Cl_4CH$	20·9	6·26
9-$HCB_{10}H_9BrCH$	14·1	4·24
9:10-$HCB_{10}H_8Br_2CH$	17·1, 18·0	5·14, 5·40
$HCB_{10}H_6Br_4CH$	21·0	6·29
9-$HCB_{10}H_9ICH$	14·0	4·20
9:10-$HCB_{10}H_8I_2CH$	18·1	5·43

Acidity constants of carboxylic acids and amines are given in Table XXIX.

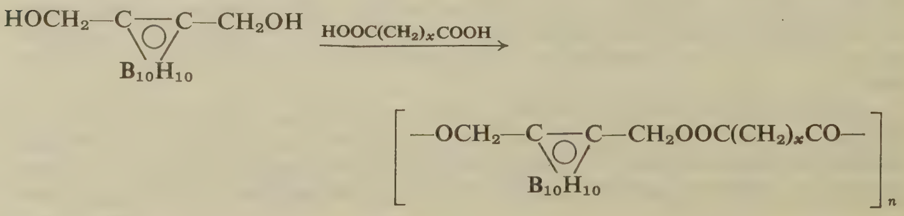
Derivatives of *Closo*-1:12-dicarbadodecaborane(12)

The published work on 1:12-$C_2B_{10}H_{12}$ systems is at present limited since the parent compound is much less readily available than its isomers. Known derivatives are listed in Table XXX. The mono- and di-lithio-reagents have been prepared together with the corresponding carboxylic acids.[276] Sulphur[412], germanium and tin derivatives[398] have been described. *B*-halogen derivatives have been obtained by isomerization of 1:7-derivatives[461], or by direct halogenation.[306, 428, 467] Direct fluorination with fluorine in hydrogen fluoride leads to 1:12-$C_2H_2B_{10}F_{10}$.[431] The ^{35}Cl nuclear-quadrapole-resonance spectrum of 1:12-C_2H_2-2-$B_{10}H_9Cl$ has been reported.[468] The dipole moment of this compound is 5·57, while that of 1:12-$C_2H_2B_{10}H_8Cl_2$ is 5·63 × 10^{-30} C m (1·69 D).[307]

Carborane Polymers

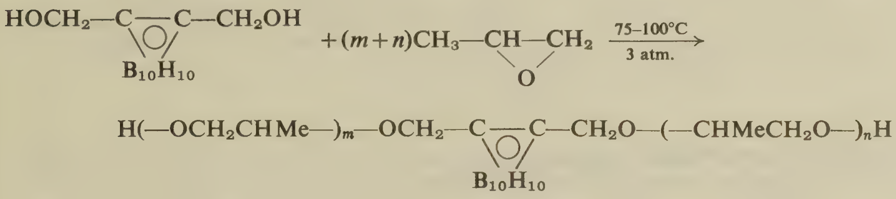
Polymers containing the 1:2-, 1:7- and 1:12-$B_{10}H_{10}C_2\langle$ groups have been the subject of considerable interest.[24, 469] These polymers are also listed in Tables XXVIII–XXX. In general it appears that, although rather more polymers of derivatives of the 1:2-isomer have been described, the polymers of the 1:7- and 1:12-isomers have the greater industrial potential.[25] These possess thermal stability at a temperature as high as 500°C and they have great resistance to atmospheric oxidation.[24, 398, 412, 457, 470–1] They also appear to have great potential as adhesives.[472–3]

Numerous polyesters have been prepared from diol, diacid, acid chloride and ester derivatives of 1:2-$C_2B_{10}H_{12}$.[474–6]

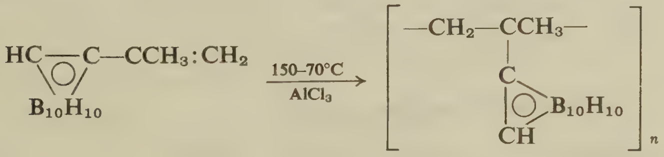


$$HOCH_2{-}C(B_{10}H_{10})C{-}CH_2OH \xrightarrow{HOOC(CH_2)_xCOOH} \left[{-}OCH_2{-}C(B_{10}H_{10})C{-}CH_2OOC(CH_2)_xCO{-}\right]_n$$

Replacement of the CH_2 groups in the diacids by CF_2 lowers the softening point of the polyesters. The bulky carborane group (van der Waals radius ≈0·4 nm) impedes the packing of molecules and the crystallization of the polymer.[319] The rate of esterification is also slower for the fluorinated acids.[477–8] The influence of the steric factor of the carborane unit is reduced by increasing the number of methylene groups between the nucleus and the functional groups. A carboranyl group can be included in the side chain of substituted malonates. This greatly inhibits polymerization of the malonate with glycols.[474] Superior polymers were obtained by co-polymerization of $B_{10}H_{10}C_2(CH_2OH)_2$, ethylene glycol and dicarboxylic acids.[475] A polydisperse, oligomeric polymer with low softening and pour points was obtained by the reaction of $B_{10}H_{10}C_2(CH_2OH)_2$ with propylene oxide[479, 480]:

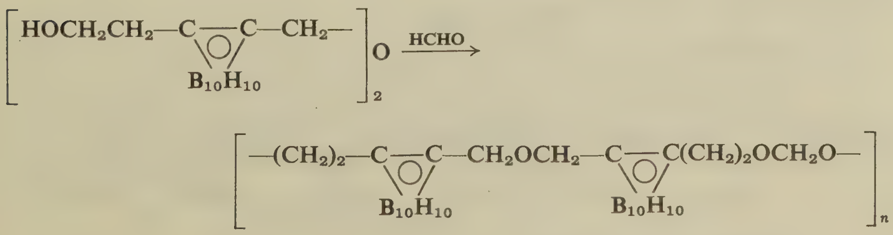


Carborane–urethane elastomers have been prepared by the reaction of di-isocyanates with carborane polyesters.[475, 479] Alkenyl-derivatives of 1:2-$C_2B_{10}H_{12}$ have proved to be rather difficult to polymerize[233], but isoprenyl-1:2-dicarbadodecaborane has been polymerized in presence of 5% aluminium chloride[481]:

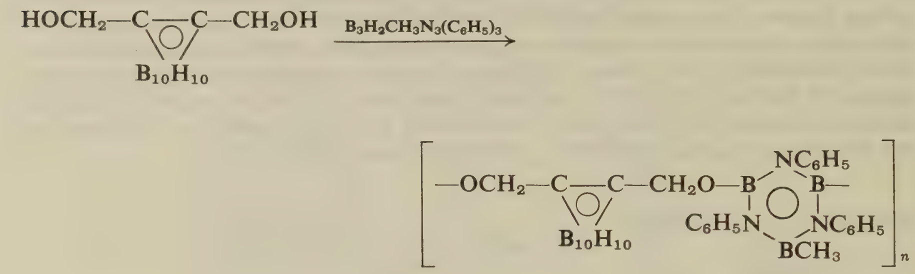


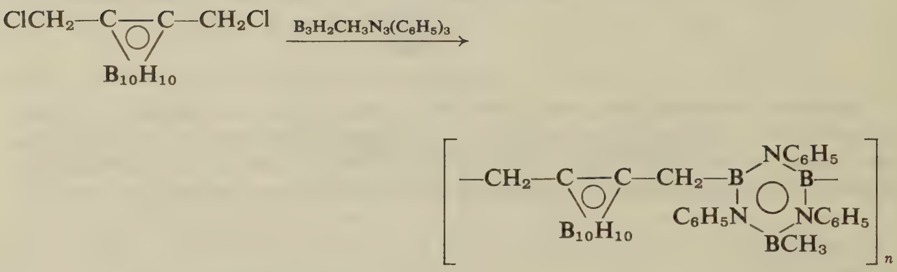
The *C*-isoprenyl-1:2-dicarbadodecaborane(12) has also been co-polymerized with methyl acrylate in presence of azo-*iso*-butyronitrile.[481]

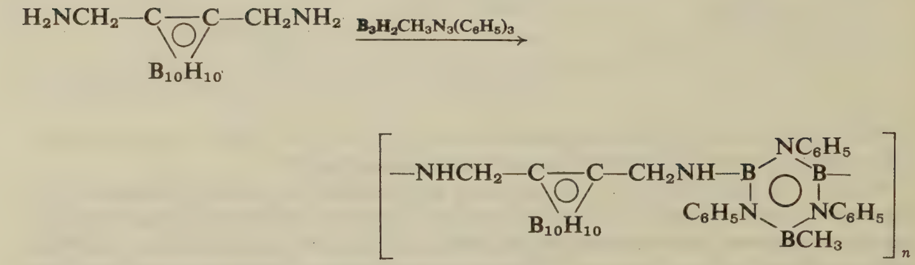
$B_{10}H_{10}C_2H.CH_2OOC.CH{:}CH_2$ has been polymerized to a brittle material which becomes elastic at 165°C. Similar radical bulk-copolymerization has been carried out in the presence of some fluorinated acrylates.[474] A polymer of mol. wt. 4400 has been obtained by the reaction of formaldehyde with a difunctional ether. This polymer has a linear structure[326]:

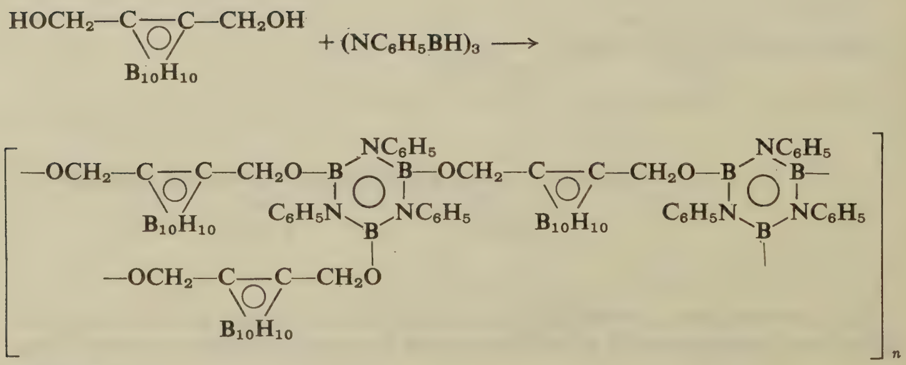


This polymer gives a rubber-like material when it is treated with 4-methyl-1:3-phenylene-di-*iso*-cyanate.[326] A polymer, which is thermally stable over 400°C, has been obtained from boric acid and $B_{10}H_{10}C_2(CH_2OH)_2$.[475] Heat- and chemical-resistant polymers have been obtained from borazole and derivatives of 1:2-$C_2B_{10}H_{12}$.[482]

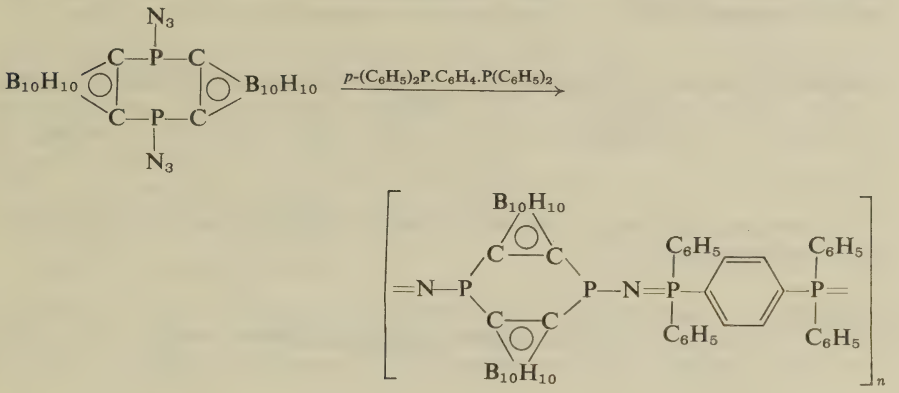




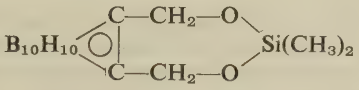




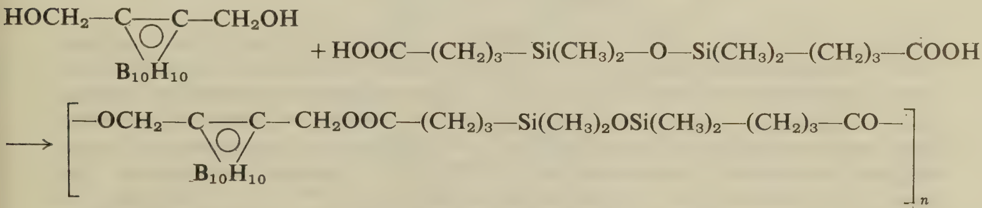
A very useful binder has been obtained from a phosphazido-exocyclic compound.[260]

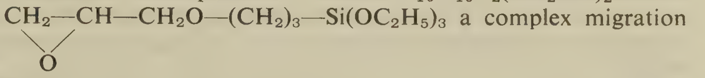


$B_{10}H_{10}C_2H(CH_2Br)$ reacts with the sodium salt of polybenzimidazole to give the very stable polymer, poly-1:2-dicarbadodecaboranylmethylbenzimidazole.[24] 1:2-Dicarbadodecaborane-siloxane polymers have been closely studied.[12, 258] The seven-membered exocyclic compound

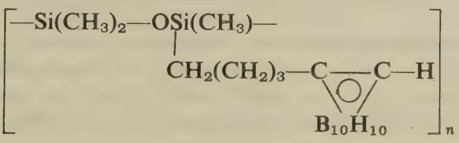


gives the parent diol and polydimethylsiloxane, $[-Si(CH_3)_2O-]_n$, on hydrolysis.[353] A series of linear carborane–siloxane polymers was prepared by the reaction of $B_{10}H_{10}C_2(CH_2OH)_2$ with dichloropolymethylsiloxanes[483], and an oligomeric product was obtained by polycondensation of the same diol with 5:5:7:7-tetramethyl-6-oxa-5:7-disilaundecane-1:11-dioic acid:

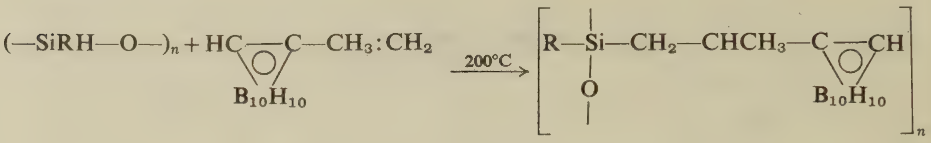


The carborane–siloxane oligomers have mol. wt. about 1000 and they are viscous liquids [8–9 Ns m^{-2} (80–90 P)], soluble in benzene and chloroform. Similar compounds have been obtained from epoxides.[484] When $B_{10}H_{10}C_2(CH_2OH)_2$ is copolymerized with  $CH_2{-}CH{-}CH_2O{-}(CH_2)_3{-}Si(OC_2H_5)_3$ a complex migration reaction occurs.[484] First, a linear polymer is formed by the reaction of the epoxy-group with the hydroxyl-groups of the carborane. In the second stage the viscous liquid becomes an elastic solid following alcoholysis of the ethoxy-groups.

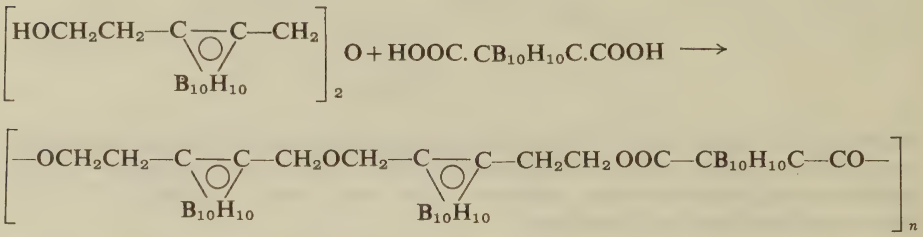
In general superior carborane–siloxane polymers are obtained when the carborane unit is in the side chain. An example is the elastic polymer of mol. wt. 13,000, which is shown below[319]:



These polymers are stable up to 450°C in air. Similar materials have been obtained by the migration co-polymerization of alkenyl derivatives of 1:2-$C_2B_{10}H_{12}$ with polyalkylsiloxanes[469, 485]:



The reaction shown below produces a vitreous mixed polymer of 1:2- and 1:7-dicarbadodecaboranes[474]:



Derivatives of 1:7-$C_2B_{10}H_{12}$ and 1:12-$C_2B_{10}H_{12}$ do not tend to form exocyclic compounds. As a result, derivatives of 1:7-$C_2B_{10}H_{12}$ have been used in the preparation of some very successful elastomeric polymers such as the 'Dexsil' series.[471, 486–9] A polysiloxane is obtained by the reaction of $(CH_3)_2ClSi—CB_{10}H_{10}C—Si(CH_3)_2Cl$ with $(CH_3)_2CH_3OSi—CB_{10}H_{10}C—SiOCH_3(CH_3)_2$ in presence of ferric chloride[394]:

$$(CH_3)_2ClSi—CB_{10}H_{10}C—Si(CH_3)_2Cl + (CH_3)_2CH_3OSi—CB_{10}H_{10}C—$$

$$SiOCH_3(CH_3)_2 \xrightarrow[140\text{–}190°C]{FeCl_3} (—Si(CH_3)_2—CB_{10}H_{10}C—Si(CH_3)_2—O—)_n$$

Analogous polymers, which have different numbers of dimethylsiloxy groups, have been obtained by the reaction of $(CH_3)_2CH_3OSi—CB_{10}H_{10}C—SiOCH_3(CH_3)_2$ with dimethyldichlorosilane, $(CH_3)_2SiCl_2$, or dichloropolymethylsiloxanes such as $Cl[Si(CH_3)_2O]_3Cl$, under similar conditions.[394] A number of interesting polymers have been prepared from derivatives of 1:7-$C_2B_{10}H_{12}$ and substituted halides of sulphur, phosphorus, germanium and tin.[398, 412, 490–1] Among the polymers that have been described are: $[—CB_{10}H_{10}C—Sn(C_6H_5)_2—]_n$[398, 457–8], $[—CB_{10}H_{10}C—Sn(CH_3)_2—]_n$[398, 457], and their germanium analogues[398, 457]; $(—CB_{10}H_{10}C—S—)_n$ and $(—S—CB_{10}H_{10}C—S—)_n$[412, 452]; and $(—CB_{10}H_{10}C—PC_6H_5—)_n$.[459] Similar polymers such as $[\text{-}(1:12)—CB_{10}H_{10}C—S—]_n$ and $[\text{-}(1:12)\text{-}CB_{10}H_{10}C—Sn(CH_3)_2—]_n$ have been obtained from the corresponding derivatives of 1:12-$C_2B_{10}H_{12}$[398, 412], whereas the corresponding derivatives of 1:2-$C_2B_{10}H_{12}$ tend to give exocyclic compounds[7]:

$$Li—CB_{10}H_{10}C—Li \xrightarrow{Sn(CH_3)_2Cl_2} [—CB_{10}H_{10}C—Sn(CH_3)_2—]_n$$

$$Li—CB_{10}H_{10}C—Li \xrightarrow{C_6H_5PCl_2} (—CB_{10}H_{10}C—PC_6H_5—)_n$$

CARBORANE–ANION COMPLEXES

One of the most fascinating aspects of the development of carborane chemistry has been the discovery of a wide range of transition-metal complexes of ions such as (3):1:2-$C_2B_9H_{11}^{2-}$ and (3):1:7-$C_2B_9H_{11}^{2-}$ which have an open pentagonal face and are *iso*-electronic with $C_5H_5^-$, the *cyclo*pentadienide ion.[21–3, 190, 306, 492–8]

Derivatives of *Nido*-(3):1:2-dicarbaundecahydroundecaborate(2−), (3):1:2-$C_2B_9H_{11}^{2-}$ and *Nido*-(3):1:7-dicarbaundecahydroundecaborate(2−), (3):1:7-$C_2B_9H_{11}^{2-}$

The $C_2B_9H_{13}$ isomers can be titrated as monobasic acids.[120,153,166] Both of the isomeric $C_2B_9H_{12}^-$ ions and their *C*-substituted derivatives react with sodium or sodium hydride in ether or tetrahydrofuran[176,178,499] to give the isomeric $C_2B_9H_{11}^{2-}$ ions (shown in Figs. 29, 30). These ions can also be generated in very concentrated aqueous solutions of alkali-metal hydroxides.[500]

The tetrahydrofuran solution of (3):1:2-$C_2B_9H_{11}^{2-}$ reacts with ferrous chloride to give a complex of Fe(III) after air oxidation.[176,178]

$$2(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}^{2-} + FeCl_2 + e \xrightarrow{C_4H_8O} 2Cl^- + [\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Fe^-$$

The ferrous analogue can be obtained from this product by reduction. If the reaction is carried out in presence of sodium *cyclo*pentadienide, the complex π-C_5H_5-Fe-π-(3):1:2-$C_2B_9H_{11}$ is obtained.[178,501] The structure of this compound (Fig. 38) has been the subject of *X*-ray investigation.[502] Analogous complexes of Co(II) and Co(III) were prepared similarly.[177,178] A list of complexes of the (3):1:2-$C_2B_9H_{11}^{2-}$ ion is given in Table XXXI. There have been published papers dealing with complexes of chromium, molybdenum and tungsten[178–9,503]; manganese and rhenium[178,499]; iron[176,178,290,500–3]; cobalt[177–8,290,433,500,503–4]; nickel and palladium[175,178,500,505–6]; copper, silver and gold[507–8]; and beryllium.[509–10] Two or even three distinct oxidation states for the central metal can usually be distinguished polarographically.[23] The detailed preparative conditions for $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Fe^-$ and $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Co^-$ have been published.[290] The Fe(III) and Co(III) complexes are stable towards acids, bases and oxidizing agents, but they are subject to electrophilic bromination[178]:

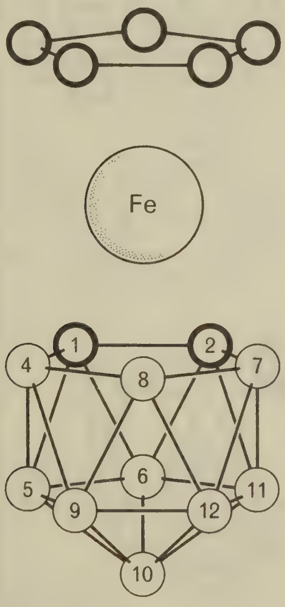


FIG. 38

$$[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Co^- + 3Br_2 \xrightarrow[CH_3COOH]{116°C} [\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_8Br_3]_2Co^-$$

The bromine atoms in this complex occupy the positions 8:9:12, and 8′:9′:12′, the three boron atoms furthest from the CoC_2 triangle.[511]

The complexes $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Cu^-$ and $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Cu^{2-}$ have the 'slipped' structures shown in Fig. 39, thus resembling π-allyl complexes.[512–13] Some of the gold, palladium and nickel complexes which have unusual oxidation states of the central metal, such as Ni(IV), also have slipped structures.[23] Complexes of $\pi\text{-}C_4(C_6H_5)_4$—Pd—[505] and many complexes of metal carbonyls have been described.[499, 514] Recently, analogous complexes of beryllium such as $\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}\text{—Be}\leftarrow O(C_2H_5)_2$ have also been described.[509]

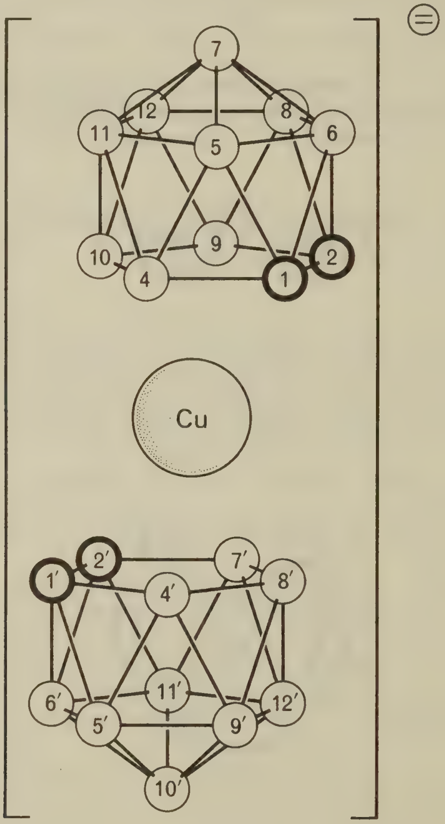


FIG. 39

Some analogous derivatives of the isomeric ligand $(3)\!:\!1\!:\!7\text{-}C_2B_9H_{11}^{2-}$ are also listed in Table XXXI.[178–9] Among physico-chemical studies there has been a theoretical calculation of the magnetic moments of these compounds[515], and *X*-ray investigations have concerned $\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}Re(CO)_3$[514], $\pi\text{-}C_5H_5\text{-Fe-}\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}$[502], $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Co^-$[516], $[8\!:\!9\!:\!12\text{-}Br_3\text{-}\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_8]_2Co^-$[511], $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Cu^-$[513] and $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Cu^{2-}$.[512] The Mössbauer spectra of some of the iron complexes have been studied[517], as has the ^{59}Co nuclear-quadrapole-resonance spectrum of $[\pi\text{-}(3)\!:\!1\!:\!2\text{-}C_2B_9H_{11}]_2Co^-$.[518] Experimental magnetic moments are listed in the Table. The iron(III) complexes have one unpaired electron [$\mu_{eff} = 17{\cdot}6\text{–}19{\cdot}4 \times 10^{-24}$ A m^2 (1·9–2·1 B.M.)] and the electron-spin resonance spectra of some of these complexes have been investigated.[519] Several polarographic studies are mentioned in Table XXXI.

Complexes of *Nido*-carbaundecahydroundecaborate(3−), $B_{10}H_{10}CH^{3-}$, and the Amine-substituted, $B_{10}H_{10}C$, [amine]$^{2-}$ Anions

These ions are isoelectronic with $C_2B_9H_{11}^{2-}$ and have been obtained similarly.[160, 520]

$$CB_{10}H_{13}^{-} \xrightarrow{2NaH} CB_{10}H_{11}^{3-}$$

$$CB_{10}H_{12}, [\text{amine}] \xrightarrow{2NaH} CB_{10}H_{10}, [\text{amine}]^{2-}$$

Several transition-metal complexes of these ions, listed in Table XXXII, have also been obtained.

Sandwich Complexes of other *Nido*-carborane Anions

When the *arachno*-carborane $C_2B_7H_{13}$ is treated with sodium hydride in ether the $C_2B_7H_{11}^{2-}$ ion is formed.[163] If this ethereal solution is treated with cobaltous chloride, an interesting redox and co-ordination reaction occurs.[163–4, 521]

$$3Co^{2+} + 4C_2B_7H_{11}^{2-} \rightarrow 2H_2 + Co\downarrow + 2(\pi\text{-}C_2B_7H_9)_2Co^-$$

Another Co(III) complex, π-C_5H_5—Co—π-$C_2B_7H_9$, was isolated in the course of this work. Proton and ^{11}B n.m.r. data indicate that there are no equivalent atoms in the $C_2B_7H_9^{2-}$ group. The structure of $(C_2B_7H_9)_2Co^-$, shown in Fig. 40, has been assigned.[23] Both of the complexes undergo a thermal rearrangement at 310°C, leading to a greater degree of symmetry (Fig. 40), with the carbon atoms in equivalent apical positions.[521] By reference to $C_2B_8H_{10}$ isomers, these isomeric $C_2B_7H_9^{2-}$ anions are formulated as (2):1:6-$C_2B_7H_9^{2-}$ and (2):1:10-$C_2B_7H_9^{2-}$. A cobalt complex of a third possible isomer, [π-(2):6:7-$C_2B_7H_9$]$_2$Co$^-$, has been reported recently.[164] A Friedel–Crafts reaction has been used to introduce an acetyl group on one of the boron atoms of the π-C_5H_5—Co—π-$C_2B_7H_9$ isomers.[522]

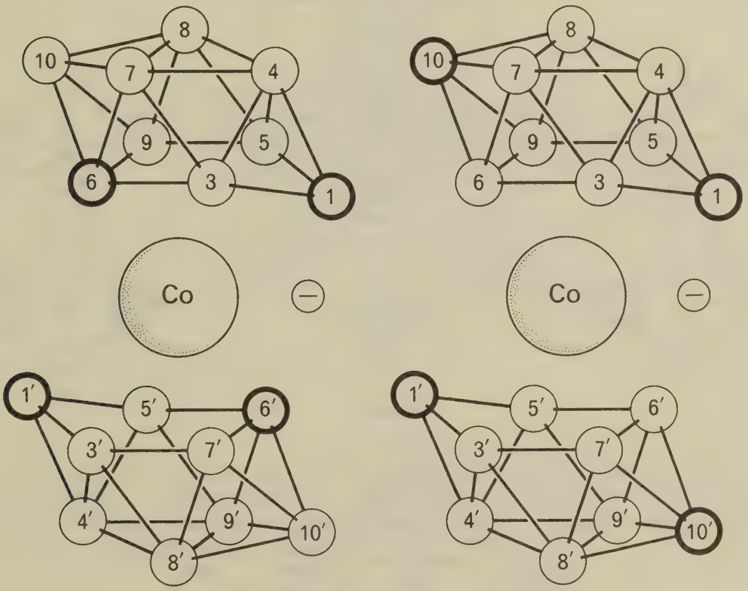


FIG. 40

When the $C_2B_7H_{11}^{2-}$ ion was reacted with $Mn(CO)_5Br$, a boron abstraction reaction occurred, and the complex π-$C_2B_6H_8Mn(CO)_3$ was obtained.[523–4] The proposed structure is shown in Fig. 41. A bright-red by-product of the aqueous preparation of [π-(3):1:2-$C_2B_9H_{11}$]$_2$Co$^-$, which contains two cobalt atoms, has been

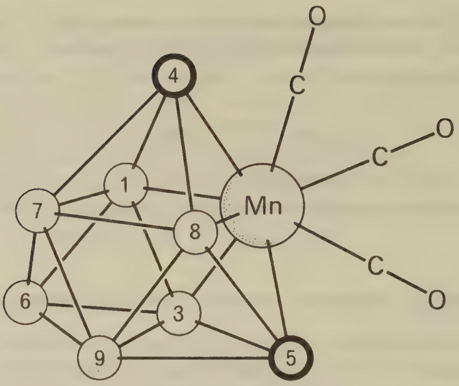


FIG. 41

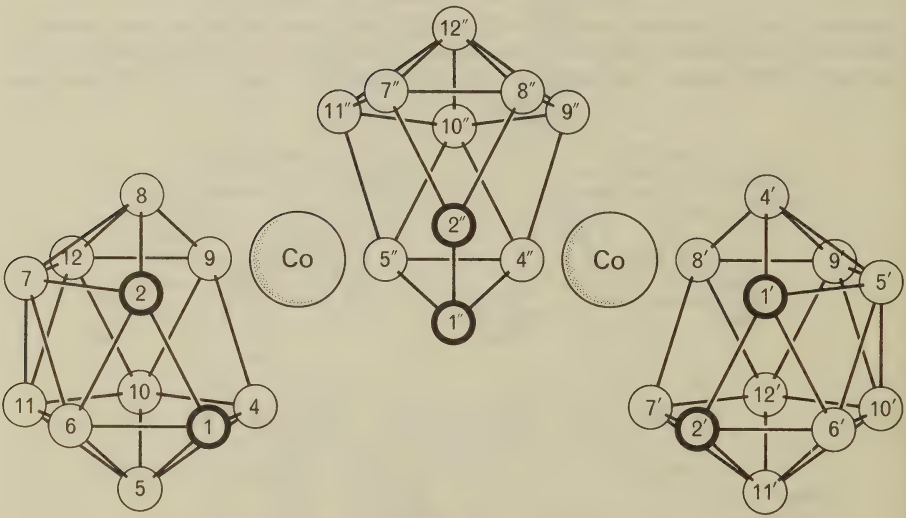


FIG. 42

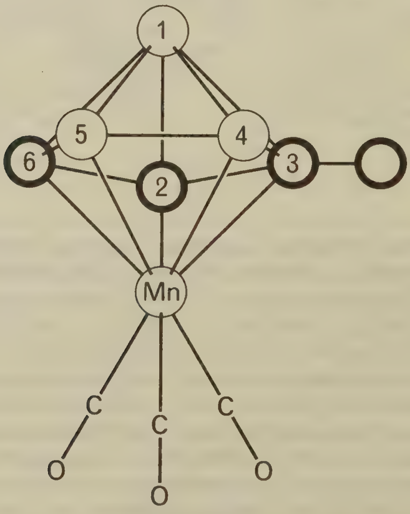


FIG. 43

isolated.[504] This compound has the remarkable structure shown in Fig. 42, containing two $C_2B_9H_{11}^{2-}$ units and a central $C_2B_8H_{10}^{4-}$ ligand.[525] The sandwich complex π-$CH_3C_3B_3H_5Mn(CO)_3$ of Fig. 43 has been isolated from the reaction of 3-CH_3.-$C_3B_3H_6$ with $Mn_2(CO)_{10}$.[526] All these complexes are listed in Table XXXIII.

ELEMENT-SUBSTITUTED CARBORANES

Recent reports describe analogues of the $C_2B_{10}H_{12}$ isomers in which a CH group is replaced by phosphorus, antimony or germanium as GeH[527–9], while in another analogue of 1:2-$C_2B_{10}H_{12}$, a BH group has been replaced by an ethylaluminium, AlC_2H_5, group.[530] The carboranes in which one atom of the nucleus has been replaced by another element are described in Table XXXIV.

Group III Substituents

1:2-C_2H_2-3-$B_9H_9.AlC_2H_5$ (Fig. 44) has been obtained by a reaction analogous to those used for boron insertion[433, 530]:

$$Na_2C_2B_9H_{11} + C_2H_5AlCl_2 \xrightarrow[-50°C]{C_4H_8O} B_9H_9.AlC_2H_5.C_2H_2,C_4H_8O$$

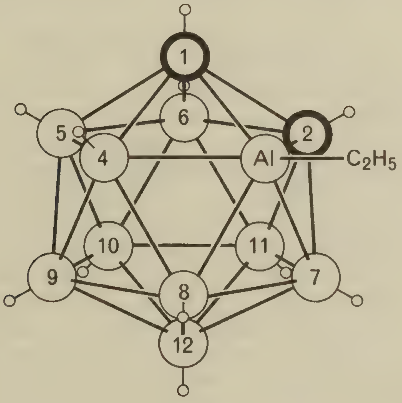


FIG. 44

A new development of considerable importance is the isolation of *closo*-1-methyl-1-gallo-2,3-dicarbaheptaborane(7), $CH_3GaC_2B_4H_6$ shown in Fig. 45. It is an analogue of $C_2B_5H_7$ with *adjacent* carbon atoms, prepared by the reaction of 4:5-$C_2B_4H_8$ with gallium trimethyl at 215°C.[531]

Group IV Substituents

1:2-$B_{10}H_{10}CHGeCH_3$ has been prepared[532] by the reaction of $Na_3B_{10}H_{10}CH$ with trimethylchlorogermane. The tetramethylammonium salt of 1:2-$B_{10}H_{10}CHGe^-$ was also obtained after this compound was treated with piperidine. 1:2-C_2H_2-3-B_9H_9Sn of Fig. 46 and analogous germanium and lead compounds, which are *iso*electronic with the presently unknown *closo*-carborane, $C_3B_9H_{11}$, have been synthesized.[533]

$$(3): 1:2\text{-}C_2B_9H_{11}^{2-} + SnCl_2 \rightarrow C_2B_9SnH_{11}$$

Silicon does not appear to have been substituted hitherto into a carborane nucleus. Compounds of formulae $(CH_3)_3SiB_5H_8$ and $(CH_3)_3SiB_5H_7Br$ have been reported[534], but these are believed to be bridge-substituted derivatives of pentaborane(9).

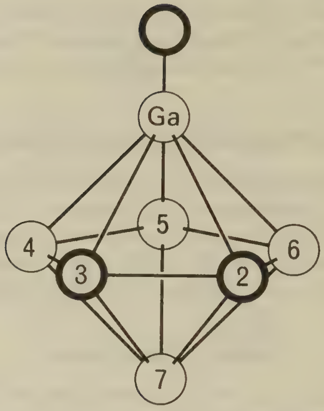


FIG. 45

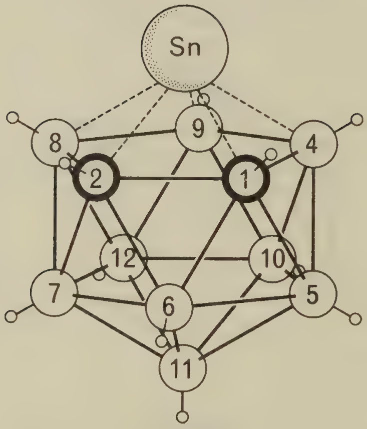


FIG. 46

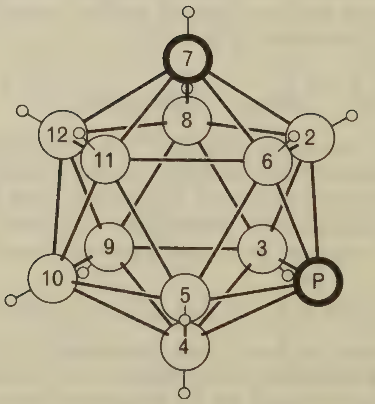


FIG. 47

Group V Substituents

An extensive series of compounds of general formula $B_{10}H_{10}CHM$ (M = P, As, Sb) and their derivatives have been prepared[535-6] by the general reaction:

$$Na_3B_{10}H_{10}CH + MCl_3 \rightarrow B_{10}H_{10}CHM$$

The 1:2-isomers can be rearranged to 1:7- and 1:12-$B_{10}H_{10}CHM$ by heating. 1:7-$CHPB_{10}H_{10}$ is depicted in Fig. 47. On treatment with piperidine the familiar boron abstraction reaction occurs for $B_{10}H_{10}CHP$ also, and gives the $C_5H_{10}NH_2^+$ derivatives of 1:2- and 1:7-$B_9H_{10}CHP^-$. These may be converted to the *p*-alkyl-*nido*-phosphacarboranes, $B_9H_{10}CHPR$, which are analogues of $C_2B_9H_{13}$. The bridge proton of these ions can be extracted with sodium hydride to give the (3):1:2- and (3):1:7-$B_9H_9CHP^{2-}$ ions, which form sandwich complexes with transition metals as discussed on p. 491. Complexes may also be obtained from the B_9H_9-$CHPCH_3^-$ ions.[537] The complex [π-(3):1:7-$B_9H_9CHPCH_3]_2Fe$ has been prepared in *meso*- and racemic forms. The racemic form has been resolved and has been the subject of *X*-ray investigation.[537] Complexes of 1:2-$B_9H_{10}CHP^-$, 1:7-$B_9H_{10}CHP^-$, 1:2-$B_9H_{10}CHAs^-$ and 1:7-$B_9H_{10}CHAs^-$ with Group VI metal carbonyls have also been reported.[538]

$$B_9H_{10}CHP^- + Mo(CO)_6 \xrightarrow{h\nu} (B_9H_{10}CHP)Mo(CO)_5^- + CO$$

CONCLUDING REMARKS

Carborane chemistry has extended rapidly during the last decade and some future developments may be anticipated. It is likely that a number of new carborane frameworks will be discovered as products of hydrocarbon–borane reactions. The limited quantities of material and the moderate thermal stability with respect to carborane interconversions are likely to remain serious practical difficulties in the study of the small carboranes, although the combined gas-chromatography/mass-spectroscopy technique has already indicated hundreds of new carboranes.[540] Conversely, the derivative chemistry of the small carboranes[541], especially that of both isomers of *closo*-dicarbadecaborane(10), will probably grow very rapidly, particularly when a high-yield synthesis of these is developed. The isomers of *closo*-dicarbadodecaborane(12) are likely to receive much attention[542-7], although it is possible that there will be few novel developments in this field beyond those of synthetic polymers.[539, 548-51] Interest in the insertion reactions of the *nido*-dicarbaundecahydroundecaborate(2−) ions and similar ions, including those derived from the sulphaboranes[552], is likely to continue, and may lead to incorporation of the majority of common elements into carborane skeletons. Furthermore, the recent interest in the development of other sandwich-bonding ligands of the carborane series may well be handsomely rewarded. These growth points are indicated by the recently published papers mentioned in this review in the form of a supplementary bibliography[553-1035] (see page 561).

Table I.—Closo-*carboranes*

Formula	Preparation references	Properties and references
1-CB_5H_7	82–4	^{11}B n.m.r. (82–3), ^{1}H n.m.r. (83), m.s. (83), i.r. (82)
1:2-$C_2B_3H_5$	Derivatives only	
1:5-$C_2B_3H_5$	9, 29, 61, 86–8, 89–95, 136	m.p. −126°C, b.p. −4°C at 760 torr, v.p. (29) i.r. (29, 87–8), m.s. (9, 29, 299) ^{11}B n.m.r. (8, 28–9, 87, 91–2, 144) ^{1}H n.m.r. (8, 29, 87, 91–2)
1:2-$C_2B_4H_6$	61, 90, 92, 94, 97, 136	m.p. −25°C, b.p. 39°C at 760 torr, i.r. (97) ^{11}B n.m.r. (8, 92, 97, 144), ^{1}H n.m.r. (92, 97) m.s. (8, 299), u.v. (94), microwave (68)
1:6-$C_2B_4H_6$	9, 61, 87, 89–95, 97–8	m.p. −32°C, b.p. 27°C at 760 torr, v.p. (97) ΔH_{vap} 25·3 kJ mole^{-1} (6·04 kcal mole^{-1}), i.r. (87, 97), ^{11}B n.m.r. (8, 87, 91–2, 97, 144), ^{1}H n.m.r. (87, 91–2, 97), m.s. (8, 97, 299)
2:4-$C_2B_5H_7$	28–9, 61, 87, 89, 91–5, 97–9	microwave (100–1), μ 4·40 × 10^{-30} C m (1·32 D) (101), i.r. (87, 102), m.s. (8, 299), ^{11}B n.m.r. (8, 87, 91–2, 102, 142, 144), ^{1}H n.m.r. (87, 91–2, 102, 142)
1:7-$C_2B_6H_8$	99, 109, 110	m.p. 30°C, ^{11}B n.m.r. (8), ^{1}H n.m.r. (109), i.r. (109)
4:5-$C_2B_7H_9$	99, 109, 112	m.p. 109°C, ^{11}B n.m.r. (8, 79), ^{1}H n.m.r. (109), i.r. (109)
1:6-$C_2B_8H_{10}$	93, 98–9, 109, 112	m.p. 106°C, ^{11}B n.m.r. (8), m.s. (8, 299), ^{1}H n.m.r. (109), i.r. (109)
1:10-$C_2B_8H_{10}$	109, 112	m.p. 162°C, ^{11}B n.m.r. (8), m.s. (8, 299), ^{1}H n.m.r. (109), i.r. (109)
2:3-$C_2B_9H_{11}$	111, 120	m.p. 212–13°C, i.r. (111), ^{11}B n.m.r. (8, 111, 121)
1:2-$C_2B_{10}H_{12}$	30–1, 81, 186, 286–90	m.p. 320°C (280–320°C if slightly impure), heat of formation −169·9 kJ mole^{-1} (−40·6 kcal mole^{-1}) (303), heat of combustion, 59·20 kJ mole^{-1} (14·15 kcal mole^{-1}) (9), electron diffraction (255), μ 14·4–15·1 × 10^{-30} C m (4·31–4·53 D) (291–5), i.r. (185, 260, 282–3, 450), Raman spectra (302), ^{11}B n.m.r. (8, 185, 241, 249, 296–8), ^{1}H n.m.r. (296), ^{13}C n.m.r. (300–1), m.s. (8, 81, 299), radiolysis (543)
1:7-$C_2B_{10}H_{12}$	9, 81, 109, 259, 304	m.p. 263–5°C, μ 9·2–9·5 × 10^{-30} C m (2·76–2·85 D) (291, 293, 295), i.r. (81, 282, 304), Raman spectrum (302), ^{11}B n.m.r. (8, 241, 249, 296–7), ^{1}H n.m.r. (296), ^{13}C n.m.r. (300–1), electron diffraction (544), m.s. (81), formation rate (305)
1:12-$C_2B_{10}H_{12}$	259, 265, 306	m.p. 259–61°C, μ 0·0 C m (295, 307), i.r. (265), ^{11}B n.m.r. (8, 265, 296–7), ^{1}H n.m.r. (296), formation rate (305)

Table II.—Closo-*carborane Anions*

Formula	Preparation references	Properties and references
1-$CB_5H_6^-$	83	^{11}B n.m.r. (83), ^{1}H n.m.r. (83), m.s. (83)
1-$CB_9H_{10}^-$	127	
2-$CB_{10}H_{11}^-$	85, 127	i.r. (85)
1-$CB_{11}H_{12}^-$	127	^{13}C n.m.r. (300)

Table III.—Nido-*carboranes and* Arachno-*carboranes*

Formula	Preparation references	Properties and references
2-CB_5H_9	66, 131, 134	i.r. (134), ^{11}B n.m.r. (131, 134)
4:5-$C_2B_4H_8$	92, 135–7	D_2, B_2D_6 exchange (147), u.v. (94), ^{11}B n.m.r. (8, 78, 92, 138–42), ^1H n.m.r. (92, 140–2), m.s. (299), i.r. (162)
1:3-$C_2B_7H_{13}$	111–12, 115, 151	m.p. 61°C, i.r. (111, 115), ^1H n.m.r. (111)
(3):1:2-$C_2B_9H_{13}$	120, 153	m.p. 110°C decomp., i.r. (153)
(3):1:7-$C_2B_9H_{13}$	120, 153	i.r. (153)
2:3:6-$C_3B_3H_7$	96, 98, 123	
3:4:5:6-$C_4B_2H_6$	Derivatives only	

Table IV.—Nido-*carborane and* Arachno-*carborane Anions*

Formula	Preparation references	Properties and references
2-$CB_5H_8^-$	Derivatives only	
$CB_5H_{10}^-$	Derivatives only	
(3):1-$CB_{10}H_{13}^-$	85	i.r. (85), ^{11}B n.m.r. (85), ^1H n.m.r. (85)
(3):1-$CB_{10}H_{11}^{3-}$	161	
4:5-$C_2B_4H_7^-$	162	^{11}B n.m.r. (162), ^1H n.m.r. (162)
$C_2B_6H_8^{2-}$	Derivatives only	
$C_2B_7H_9^{2-}$	Derivatives only	
1:3-$C_2B_7H_{11}^{2-}$	163–5, 171	
1:3-$C_2B_7H_{12}^-$	Derivatives only	
$C_2B_8H_{10}^{4-}$	Derivatives only	
(3):1:2-$C_2B_9H_{11}^{2-}$	178	
(3):1:7-$C_2B_9H_{11}^{2-}$	178–9	i.r. (179), u.v. (179)
(3):1:2-$C_2B_9H_{12}^-$	119, 153, 167	m.p. (picoline$^+$ salt) > 300°C, i.r. (119, 153), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
(3):1:7-$C_2B_9H_{12}^-$	119, 151, 188	m.p. (Cs^+ salt) 328°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
1:2-$C_2B_{10}H_{12}^{2-}$	Derivatives only	
2:3:6-$C_3B_3H_6^-$	Derivatives only	

Table V.—Closo-*monocarborane Derivatives*

Formula	Preparation references	Properties and references
$B_{10}H_{10}C.N(CH_3)_3$	85	m.p. 333–4°C, i.r. (85), ^{11}B n.m.r. (85), ^1H n.m.r. (85)
$B_{10}H_{10}CN(CH_3)_2$*n*-C_3H_7	85	m.p. 179–81°C, i.r. (85)

Table VI.—Closo-*dicarbapentaborane*(5) *Derivatives*

Formula	Preparation references	Properties and references
2-CH_3-1:2-$C_2B_3H_4$	88	i.r. (88)
C:3-$(CH_3)_2$-1:2-$C_2B_3H_3$	86–8	i.r. (86–8), ^{11}B n.m.r. (86–7), ^{1}H n.m.r. (86–7)
C:5-$(CH_3)_2$-1:2-$C_2B_3H_3$	88	^{1}H n.m.r. (88), i.r. (88)
C:3:5-$(CH_3)_3$-1:2-$C_2B_3H_2$	88	i.r. (88)
3:4:5-$(CH_3)_3$-1:2-$C_2B_3H_2$	88	i.r. (88)
C:3:4:5-$(CH_3)_4$-1:2-C_2B_3H	88	i.r. (88)
C':3:4:5-$(CH_3)_4$-1:2-C_2B_3H	88	i.r. (88)
1:5-$C_2B_3H_3D_2$	29	i.r. (29), m.s. (29)
1:5-$C_2H_2B_3D_3$	29	i.r. (29), m.s. (29)
1:5-$C_2B_3D_5$	29	i.r. (29), m.s. (29)
1:5-$C_2{}^{10}B_3H_5$	29	m.s. (29)
2-CH_3-1:5-$C_2B_3H_4$	86–7, 93, 98	i.r. (87), ^{11}B n.m.r. (87), ^{1}H n.m.r. (87)
C:3-$(CH_3)_2$-1:5-$C_2B_3H_3$	93	
2:3-$(CH_3)_2$-1:5-$C_2B_3H_3$	87, 91	i.r. (87), ^{11}B n.m.r. (91), ^{1}H n.m.r. (91)
n-Pr-1:5-$C_2B_3H_4$	91	^{11}B n.m.r. (91), ^{1}H n.m.r. (91)
$(C_2H_5)_4C_2B_3H$	63	
$(CH_3)_2(C_2H_5)_3C_2B_3$	105, 107, 126	m.p. −84°C, b.p. 58°C at 11 torr, n_D^{20} 1·4385, d_4^{20} 0·7697, ^{1}H n.m.r. (422), Raman spectrum (422)
$(C_2H_5)_5C_2B_3$	125	m.p. −62°C, b.p. 84–6°C at 9 torr
$(C_2H_5)_2(n\text{-}C_3H_7)_3C_2B_3$	125	b.p. 117–18°C at 10 torr
$(C_2H_5)_4(iso\text{-}C_4H_9)C_2B_3$	125	

Table VII.—Closo-*dicarbahexaborane*(6) *Derivatives*

Formula	Preparation references	Properties and references
1:6-$C_2B_4H_4D_2$	97	i.r. (97), m.s. (97)
1:6-$C_2B_4H_2D_4$	97	i.r. (97), m.s. (97)
1:6-$C_2B_4D_6$	97	i.r. (97), m.s. (97)
1:6-$C_2B_4{}^{10}H_6$	97	i.r. (97), m.s. (97)
1-CH_3-1:6-$C_2B_4H_5$	93	
2-CH_3-1:6-$C_2B_4H_5$	87	i.r. (87), ^{11}B n.m.r. (87), ^{1}H n.m.r. (87)
$(CH_3)_2$-1:6-$C_2B_4H_4$	91	m.p. −2°C, ^{11}B n.m.r. (91), ^{1}H n.m.r. (91)
n-C_3H_7-1:6-$C_2B_4H_5$	91	m.p. −88°C, ^{11}B n.m.r. (91), ^{1}H n.m.r. (91)
$(CH_3)_2(C_2H_5)_4C_2B_4$	63	

Table VIII.—Closo-*dicarbaheptaborane*(7) *Derivatives*

Formula	Preparation references	Properties and references
3:5:6-D_3-2:4-$C_2B_5H_4$	102	^{1}H n.m.r. (102)
2:4-$C_2H_2B_5D_5$	102	^{1}H n.m.r. (102)
1-CH_3-2:4-$C_2B_5H_6$	87, 93, 98	i.r. (87), ^{11}B n.m.r. (87), ^{1}H n.m.r. (87)
3-CH_3-2:4-$C_2B_5H_6$	87, 93, 98	i.r. (87), ^{11}B n.m.r. (87), ^{1}H n.m.r. (87)
5-CH_3-2:4-$C_2B_5H_6$	87, 93, 98	i.r. (87), ^{11}B n.m.r. (87), ^{1}H n.m.r. (87)
CH_3-2:4-$C_2B_4H_6$	93, 98–9	m.s. (299)
1:7-$(CH_3)_2$-2:4-$C_2B_5H_5$	93	
$(CH_3)_2$-2:4-$C_2B_5H_5$	99	m.p. −29°C
2:4-$C_2H_2B_5(CH_3)_5$	108	i.r. (108), ^{11}B n.m.r. (108)
1-C_2H_5-2:4-$C_2B_5H_6$	93	
n-C_3H_7-2:4-$C_2B_5H_6$	1	m.p. −98°C
$(CH_3)_2(C_2H_5)_3C_2B_5H_2$	105, 107	
$CH_3(C_2H_5)_4C_2B_5H_2$	104	
$(C_2H_5)_5C_2B_5H_2$	104	
$(CH_3)_2(C_2H_5)_4C_2B_5H$	105, 107	
$CH_3(C_2H_5)_5C_2B_5H$	106	b.p. 65–7°C at 0·001 torr, i.r. (106), ^{11}B n.m.r. (106), ^{1}H n.m.r. (106)
$(CH_3)_3(C_2H_5)_4C_2B_5$	104	
2:4-$C_2(CH_3)_2B_5(C_2H_5)_5$	63, 103–4, 106–7, 187	m.p. 87°C, i.r. (106), ^{11}B n.m.r. (106), ^{1}H n.m.r. (106)

Table IX.—Closo-*dicarbaoctaborane*(8) *Derivatives*

Formula	Preparation references	Properties and references
CH_3-1:7-$C_2B_6H_7$	99, 109	b.p. 102°C, ^{1}H n.m.r. (109), i.r. (109)
1:7-$C_2(CH_3)_2B_6H_6$	78–9, 99, 111–12	m.p. −40°C, b.p. 62°C at 134 torr, ^{11}B n.m.r. (79, 111), m.s. (8, 78, 299), *X*-ray (113–14)
C_6H_5-1:7-$C_2B_6H_7$	109	b.p. 234°C, ^{1}H n.m.r. (109), i.r. (109)

Table X.—Closo-*dicarbanonaborane*(9) *Derivatives*

Formula	Preparation references	Properties and references
CH_3-4:5-$C_2B_7H_8$	99, 109	b.p. 139°C, ^{1}H n.m.r. (109), i.r. (109)
CH_3-4:5-$C_2B_7H_8$	109	
4:5-$C_2(CH_3)_2B_7H_7$	79, 99, 111–12	m.p. −22°C, ^{11}B n.m.r. (79, 111), m.s. (8, 299), *X*-ray (116)
C_6H_5-4:5-$C_2B_7H_8$	109	m.p. 38°C, ^{1}H n.m.r. (109), i.r. (109)

Table XI.—Closo-*dicarbadecaborane*(10) *Derivatives*

Formula	Preparation references	Properties and references
1-(CH_3)-1:6-$C_2B_8H_9$	165	
6-(CH_3)-1:6-$C_2B_8H_9$	165	
B-(CH_3)-1:6-$C_2B_8H_9$	93, 98	
(CH_3)-1:6-$C_2B_8H_9$	99, 109	b.p. 165°C, ^{1}H n.m.r. (109), i.r. (109)
$(CH_3)_2$-1:6-$C_2B_8H_8$	79, 99, 111–12	m.p. 1–2°C, b.p. 73°C at 32 torr, ^{11}B n.m.r. (79, 111), m.s. (299)
C_6H_5-1:6-$C_2B_8H_9$	109	m.p. 51°C, ^{1}H n.m.r. (109), i.r. (109)
1:6-C_2CH_3-C_6H_5-B_8H_8	165	b.p. 280–1°C at 760 torr
CH_3-1:10-$C_2B_8H_9$	109	m.p. 40°C, ^{1}H n.m.r. (109), i.r. (109)
$(CH_3)_2$-1:10-$C_2B_8H_8$	79, 111–12, 165	m.p. 26–8°C, ^{11}B n.m.r. (79, 111), m.s. (299)
C_6H_5-1:10-$C_2B_8H_9$	109	m.p. 43°C, ^{1}H n.m.r. (109), i.r. (109)
1:10-C_2CH_3-C_6H_5-B_8H_8	165	m.p. 36–7°C
1:10-$B_8H_8C_2CH_3I$	165	m.p. 61–2°C
1:10-$B_8H_8C_2CH_3$.COOH	165	m.p. 156–7°C
1:10-$B_8H_8C_2$-C_6H_5-COOH	165	m.p. 192–4°C
1:10-$B_8H_8C_2(COOH)_2$	165	m.p. 316–17°C
1:10-$B_8H_8C_2$-C_6H_5-NH_2	165	m.p. 106–8°C
4-(1:10-$B_8H_8C_2H$)-2:3-$C_2B_9H_{10}$	118	m.p. 116–18°C, i.r. (118), ^{11}B n.m.r. (118), ^{1}H n.m.r. (118)
4-(1:10-$B_8H_8C_2H$)-(3):1:7-$C_2B_9H_{11}^-$	118	m.p. (Cs^+ salt) 233–6°C, i.r. (118), ^{11}B n.m.r. (118), ^{1}H n.m.r. (118)
4-(1:10-$B_8H_8C_2(C_2H_5)$)-(3):1:7-$C_2B_9H_{11}^-$	118	m.p. (Cs^+ salt) 342–6°C, i.r. (118), ^{11}B n.m.r. (118), ^{1}H n.m.r. (118)
1:10-$B_8Cl_8C_2H_2$	165	m.p. 179–80°C
1:10-$B_8Cl_8C_2(CCl_3)_2$	165	m.p. 213–15°C
1:10-$B_8H_8C_2(Fe(CO)_2$-$(C_5H_5))_2$	128, 492	m.p. 203–4°C, ^{1}H n.m.r. (128), u.v. (128)

Table XII.—Closo-*dicarbaundecaborane*(11) *Derivatives*

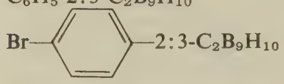
Formula	Preparation references	Properties and references
CH_3-2:3-$C_2B_9H_{10}$	111, 120	m.p. 84–5°C, i.r. (111)
$(CH_3)_2$-2:3-$C_2B_9H_9$	111, 120	m.p. 57–8°C, i.r. (111), *X*-ray (122)
C_6H_5-2:3-$C_2B_9H_{10}$	111, 120, 166	i.r. (111), m.p. 37–8°C
	111	m.p. 101°C, i.r. (111)
$(CH_3)_2$-2:3-$C_2B_9H_9OH^-$	111	i.r. (111)
4-(1:10-$B_8H_8C_2H$)-2:3-$C_2B_9H_{10}$	118	m.p. 116–18°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2H$)-2:3-$C_2B_9H_{10}$	118	m.p. 156–8°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2CH_3$)-2:3-$C_2B_9H_{10}$	118	m.p. 116–18°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2H$)-2:3-$C_2(CH_3)_2B_9H_8$	118	m.p. 82–3°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2CH_3$)-2:3-$C_2(CH_3)_2B_9H_8$	118	m.p. 101–2°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
(2:3-$C_2B_9H_{10})_2CoS_2CH$	129	^1H n.m.r. (129), *X*-ray (129)
(2:3-$C_2B_9H_{10})_2CoS_2C^-$	129	

Table XIII.—Closo-*carborane Metal Derivatives*

Formula	Preparation references	Properties and references
(2:3-$C_2B_9H_{10})_2CoS_2CH$	129	^1H n.m.r. (129), *X*-ray (129)
(2:3-$C_2B_9H_{10})_2CoS_2C^-$	129	
1:10-$B_8H_8C_2[Fe(CO)_2(C_5H_5)]_2$	128, 492	m.p. 203–4°C, ^1H n.m.r. (128), u.v. (128)

Table XIV.—Arachno- *and* Nido-*monocarborane Derivatives*

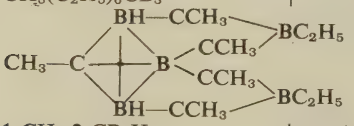
Formula	Preparation references	Properties and references
$CH_3(C_2H_5)_6CB_3$	130	
 BH—CCH_3 BC_2H_5 CCH_3 CH_3—C B CCH_3 BC_2H_5 BH—CCH_3	130	m.s. (124)
1-CH_3-2-CB_5H_8	131, 134	i.r. (134), ^{11}B n.m.r. (131, 134)
2-CH_3-2-CB_5H_8	66, 132–4	i.r. (132, 134), ^{11}B n.m.r. (8, 133–4), m.s. (133, 299), u.v. (94)
3-CH_3-2-CB_5H_8	133–4	i.r. (134), ^{11}B n.m.r. (133–4), m.s. (133)
4-CH_3-2-CB_5H_8	98, 133	^{11}B n.m.r. (133), m.s. (133)
1:2-$(CH_3)_2$-2-CB_5H_7	132, 134	i.r. (132, 134), ^{11}B n.m.r. (134)
1:3-$(CH_3)_2$-2-CB_5H_7	134	i.r. (134), ^{11}B n.m.r. (134)
2:3-$(CH_3)_2$-2-CB_5H_7	132, 134	i.r. (132, 134), ^{11}B n.m.r. (134)
1:2:3-$(CH_3)_3$-2-CB_5H_6	134	i.r. (134), ^{11}B n.m.r. (134)
2-C_2H_5-2-CB_5H_8	84	i.r. (84), ^{11}B n.m.r. (84), ^1H n.m.r. (84)
1-C_2H_5:2-CH_3-2-CB_5H_7	134	i.r. (134), ^{11}B n.m.r. (134)
2-CH_3:3-C_2H_5-2-CB_5H_7	134	i.r. (134), ^{11}B n.m.r. (134)
$CH_3(C_2H_5)_4CB_5H_4$	159	i.r. (159), ^{11}B n.m.r. (159), ^1H n.m.r. (159)
$CH_3(C_2H_5)_5CB_5H_3$	107, 126	

Table XV.—Nido-*dicarbahexaborane Derivatives*

Formula	Preparation references	Properties and references
μ-D-4:5-$C_2B_4H_7$	162	i.r. (162), ^{11}B n.m.r. (162)
D_2-4:5-$C_2B_4H_6$	147	
D_3-4:5-$C_2B_4H_5$	162	i.r. (162), m.s. (162)
1-CH_3-4:5-$C_2B_4H_7$	148	^{11}B n.m.r. (148), ^1H n.m.r. (148)
2-CH_3-4:5-$C_2B_4H_7$	148	^{11}B n.m.r. (148), ^1H n.m.r. (148)
3-CH_3-4:5-$C_2B_4H_7$	148	^{11}B n.m.r. (148), ^1H n.m.r. (148)
4-CH_3-4:5-$C_2B_4H_7$	84, 92, 132, 138	i.r. (132), ^{11}B n.m.r. (92, 138), ^1H n.m.r. (92)
4:5-$(CH_3)_2$-4:5-$C_2B_4H_6$	92, 138	m.p. −64°C, b.p. 25°C at 29 torr, i.r. (132), ^{11}B n.m.r. (92, 132, 138–9, 141–2), u.v. (94), ^1H n.m.r. (92, 132, 141–2), *X*-ray (145–6), D_2, DCl-exchange (162)
1:4:5-$(CH_3)_3$-4:5-$C_2B_4H_5$	148	^{11}B n.m.r. (148), ^1H n.m.r. (148)
3:4:5-$(CH_3)_3$-4:5-$C_2B_4H_5$	148	^{11}B n.m.r. (148), ^1H n.m.r. (148)
B-CH_3-4:5-$C_2B_4H_7$	141	^{11}B n.m.r. (141), ^1H n.m.r. (141)
B:4:5-$(CH_3)_3$-4:5-$C_2B_4H_5$	141	^{11}B n.m.r. (141), ^1H n.m.r. (141)
$(CH_3)_2C_2B_4H_6$	93	
$(n\text{-}C_3H_7)_2$-4:5-$C_2B_4H_6$	138	^{11}B n.m.r. (138, 139)
C_6H_5-4:5-$C_2B_4H_7$	92	^{11}B n.m.r. (92), ^1H n.m.r. (92), u.v. (92)
$CH_2{=}CCH_3$-4:5-$C_2B_4H_7$	92	^{11}B n.m.r. (92), ^1H n.m.r. (92)
3-Cl-4:5-$C_2B_4H_7$	149–50	m.p. −73°C, v.p. (149), i.r. (149), ^{11}B n.m.r. (149), ^1H n.m.r. (149)
3-Br-4:5-$C_2B_4H_7$	149–50	m.p. −69°C, v.p. (149), i.r. (149), ^{11}B n.m.r. (149), ^1H n.m.r. (149)

Table XVI.—Arachno-*dicarbanonaborane Derivatives*

Formula	Preparation references	Properties and references
CH_3-1:3-$C_2B_7H_{12}$	99, 111, 115	m.p. 23–4°C, i.r. (111, 115), ^1H n.m.r. (111)
1:3-$(CH_3)_2$-1:3-$C_2B_7H_{11}$	99, 111, 115	m.p. 50–2°C, i.r. (111, 115), ^{11}B n.m.r. (115) ^1H n.m.r. (111), *X*-ray (152)
C_6H_5-1:3-$C_2B_7H_{12}$	111, 115	m.p. 77–9°C, i.r. (111), ^{11}B n.m.r. (111)
CH_3-1:3-$C_2B_7H_{10}D_2$	115	
CH_3-1:3-$C_2B_7H_8D_4$	115	
$(CH_3)_2$-1:3-$C_2B_7H_{10}D$	115	
$(CH_3)_2$-1:3-$C_2B_7H_9D_2$	164	

Table XVII.—Nido-*dicarbaundecaborane Derivatives*

Formula	Preparation references	Properties
C_6H_5-$C_2B_9H_{12}$	154	
$C_2B_9H_{12}I$	169	70–1°C

Table XVIII.—Nido-*tricarbaborane Derivatives*

Formula	Preparation references	Properties and references
$3\text{-}CH_3\text{-}2{:}3{:}6\text{-}C_3B_3H_6$	98, 123, 132	i.r. (98), ^{11}B n.m.r. (123), ^{1}H n.m.r. (123)
$2{:}3\text{-}(CH_3)_2\text{-}2{:}3{:}6\text{-}C_3B_3H_5$	98, 123	i.r. (98), ^{11}B n.m.r. (123), ^{1}H n.m.r. (123)
$3{:}6\text{-}(CH_3)_2\text{-}2{:}3{:}6\text{-}C_3B_3H_5$	98, 123, 132	i.r. (98), ^{11}B n.m.r. (123), ^{1}H n.m.r. (123)
$2{:}3\text{-}(CH_3)_2\text{-}6\text{-}C_2H_5\text{-}2{:}3{:}6\text{-}C_3B_3H_4$	132	i.r. (132)
$\mu\text{-D-}3{:}6\text{-}(CH_3)_2\text{-}2{:}3{:}6\text{-}C_3B_3H_4$	155, 184	i.r. (184), ^{11}B n.m.r. (184), ^{1}H n.m.r. (184)
$(CH_3)_3(C_2H_5)_3C_3B_3H$	63	

Table XIX.—Nido-*tetracarborane Derivatives*

Formula	Preparation references	Properties
$(CH_3)_2(C_2H_5)_4C_4B_2$	156	
$(C_2H_5)_6C_4B_2$	156	
$(C_6H_5)_6C_4B_2$	157–8	m.p. 146–9°C

Table XX.—Smaller Nido-*carborane anion Derivatives*

Formula	Preparation references	Properties and references
$CH_3(C_2H_5)_5CB_5H_2^-$	159	
$CH_3(C_2H_5)_5CB_5H_4^-$	159	
$CB_{10}H_{11}Cl_2^-$	85	i.r. (85)
$CB_{10}H_{12}Br^-$	85	i.r. (85)
$CB_{10}H_{11}Br_2^-$	85	i.r. (85)
$(CH_3)_2\text{-}4{:}5\text{-}C_2B_4H_5^-$	162	^{11}B n.m.r. (162), ^{1}H n.m.r. (162)
$(CH_3)_2\text{-}1{:}3\text{-}C_2B_7H_9^{2-}$	164	
$(CH_3)_2\text{-}1{:}3\text{-}C_2B_7H_{10}^-$	115, 165	
$C_6H_5\text{-}1{:}3\text{-}C_2B_7H_{10}^{2-}$	164	
$(CH_3)_2\text{-}2{:}3{:}6\text{-}C_3B_3H_4^-$	155, 184	

Table XXI.—Nido-(3):1:2-*dicarbadodecahydroundecaborate*(1 −), (3):1:2-$C_2B_9H_{12}^-$ *Derivatives*

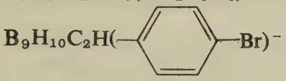
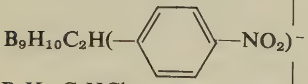
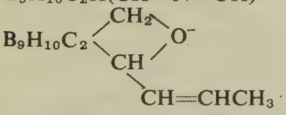
Formula	Preparation references	Properties and references
$B_9H_{10}C_2(CH_3)_2^-$	119, 178, 290	i.r. (119, 290), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
$B_9H_{10}C_2HC_6H_5^-$	119, 167, 178, 188	$(CH_3)_4N^+$ salt: m.p. 257–9°C, $CH_3C_5H_4N^+$ salt: m.p. 122–3°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119), optical resolution (119)
$B_9H_{10}C_2H(CH{=}CH_2)^-$	167, 188	
$B_9H_{10}C_2CH_3C_6H_5^-$	119	m.p. ($CH_3C_5H_4N^+$ salt) 154–5°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119), optical resolution (119)
$B_9H_{10}C_2CH_3(CH_2C_6H_5)^-$	327	$(CH_3)_4N^+$ salt: m.p. 167–9°C
	119	Cs^+ salt: m.p. 277–9°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
	167	$CH_3C_5H_4N^+$ salt: m.p. 155–6°C
$B_9H_{10}C_2HCl^-$	378	$CH_3C_5H_4N^+$ salt: m.p. 127–8°C
$B_9H_{10}C_2C_6H_5Cl^-$	167, 188	$CH_3C_5H_4N^+$ salt: m.p. 126–8°C
$B_9H_{10}C_2C_6H_5CN^-$	332	$CH_3C_5H_4N^+$ salt: m.p. 97–9°C
$B_9H_{10}C_2H(CH{=}N{-}OH)^-$	327	
	167, 188	$CH_3C_5H_4N^+$ salt: m.p. 138–40°C
6-C_2H_5-$B_9H_9C_2H_2^-$	433	$(CH_3)_4N^+$ salt: m.p. 278–9°C decomp., ^1H n.m.r. (433)
6-C_6H_5-$B_9H_9C_2H_2^-$	433–4	$(CH_3)_4N^+$ salt: m.p. 132–3°C, ^{11}B n.m.r. (434), ^1H n.m.r. (433–4)
6-C_6H_5-$B_9H_9C_2(CH_3)_2$	433	$(CH_3)_4N^+$ salt: m.p. 283–6°C decomp., ^1H n.m.r. (433)
$B_9H_9BrC_2(CH_3)_2^-$	169	^{11} B n.m.r. (169), u.v. (169)
$B_9H_6Br_4C_2H_2^-$	292	$CH_3(C_6H_5)_3N^+$ salt: m.p. 151–2°C
$B_9H_9IC_2H_2^-$	169	^{11}B n.m.r. (169), u.v. (169)
$B_9H_9IC_2HCH_3^-$	169	^{11}B n.m.r. (169), u.v. (169)
$B_9H_9IC_2(CH_3)_2^-$	169	^{11}B n.m.r. (169), u.v. (169)
$B_9H_9IC_2HC_6H_5^-$	169	^{11}B n.m.r. (169), u.v. (169)
$B_9H_9{}^{131}IC_2H_2^-$	441	
$B_9H_8{}^{131}I_2C_2H_2^-$	441	

Table XXII.—Nido-(3):1:7-*dicarbadodecahydroundecaborate*(1 −), (3):1:7-$C_2B_9H_{12}^-$ *Derivatives*

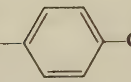
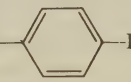
Formula	Preparation references	Properties and references
$HCB_9H_{10}CCH_3^-$	171, 175	$CH_3C_5H_4N^+$ salt: m.p. 207–8°C, i.r. (175), ^{11}B n.m.r. (175), ^1H n.m.r. (175)
$HCB_9H_{10}CC_6H_5^-$	119, 166, 170, 171, 174	Cs^+ salt: m.p. 353–5°C decomp., $CH_3C_5H_4N^+$ salt: m.p. 93–5°C, i.r. (119, 166), ^{11}B n.m.r. (119), ^1H n.m.r. (119), optical resolution (119)
$HCB_9H_{10}C$—  —Cl^-	170	$CH_3C_5H_4N^+$ salt: m.p. 152–4°C
$HCB_9H_{10}C$—  —Br^-	170	
4-CH_3-$(HCB_9H_9CH)^-$	118	$(CH_3)_4N^+$ salt: m.p. 354–5°C decomp.
4-(*n*-C_4H_9)-$(HCB_9H_9CH)^-$	118	$(CH_3)_4N^+$ salt: m.p. 282–5°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
9:10-Br_2-$(HCB_9H_8CH)^-$	171	$CH_3C_5H_4N^+$ salt: m.p. 170–2°C
4-$[(CH_3OOC)_2CH](HCB_9H_9CH)^-$	118	$(CH_3)_4N^+$ salt: m.p. 239–40°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-$[(CN)_2CH](HCB_9H_9CH)^-$	118	$(CH_3)_4N^+$ salt: m.p. 159–61°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:10-$B_8H_8C_2H)(CH_3CB_9H_9CCH_3)^-$	118	Cs^+ salt: m.p. 233–6°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:10-$B_8H_8C_2C_2H_5)(CH_3CB_9H_9CCH_3)^-$	118	Cs^+ salt: m.p. 342–6°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:10-$B_8H_8C_2C_6H_5)(HCB_9H_9CH)^-$	175	i.r. (175), ^{11}B n.m.r. (175), ^1H n.m.r. (175)
4-(1:2-$B_{10}H_{10}C_2H)(HCB_9H_9CH)^-$	118	Cs^+ salt: m.p. >360°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2H)(CH_3CB_9H_9CCH_3)^-$	118	Cs^+ salt: m.p. 244–6°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)
4-(1:2-$B_{10}H_{10}C_2CH_3)(HCB_9H_9CH)^-$	118, 175	$(CH_3)_4N^+$ salt: m.p. >360°C, i.r. (118, 175), ^{11}B n.m.r. (118, 175), ^1H n.m.r. (118, 175)
4-(1:2-$B_{10}H_{10}C_2CH_3)(CH_3CB_9H_9CCH_3)^-$	118	Cs^+ salt: m.p. 229–31°C, i.r. (118), ^{11}B n.m.r. (118), ^1H n.m.r. (118)

Table XXIII.—Derivatives of the nido-*dicarbaundecahydroundecaborate*(2 −), $C_2B_9H_{11}^{2-}$ *ions*

Formula	Preparation references
(3):1:2-$B_9H_9C_2(CH_3)_2^{2-}$	178
(3):1:2-$B_9H_9C_2HC_6H_5^{2-}$	178
6-C_6H_5-(3):1:2-$C_2B_9H_{10}^{2-}$	433
6-C_6H_5-(3):1:2-$B_9H_8C_2(CH_3)_2^{2-}$	433

Table XXIV.—Derivatives of the nido-*dicarbadodecahydrododecaborate*(2 −), $C_2B_{10}H_{12}^{2-}$, *and* nido-*tridecahydrododecaborate*(1 −), $C_2B_{10}H_{13}^-$ *ions*

Formula	Preparation references	Properties
1:2-$B_{10}H_{10}C_2(C_6H_5)_2^{2-}$	182, 268	$CH_3C_5H_4N^+$ salt: m.p. 159–61°C
1:2-$B_{10}H_{11}C_2(C_6H_5)_2^-$	182	$CH_3C_5H_4N^+$ salt: m.p. 161–2°C
1:2-$B_{10}H_{10}CH_3C_2HC_6H_5^-$	181	$CH_3C_5H_4N^+$ salt: m.p. 111–12°C
1:2-$B_{10}H_{10}C_2H_5C_2HC_6H_5^-$	181	$CH_3C_5H_4N^+$ salt: m.p. 120–2°C

Table XXV.—$C_2B_9H_{13}$, *Ligand Complexes and Associated Compounds**

Formula	Preparation references	Properties and references
1:2-$C_2B_9H_{13}$,N_2H_4	186	
1:2-$C_2B_9H_{13}$,$N(CH_3)_3$	119	m.p. 308–10°C, i.r. 119, ^{11}B n.m.r. (119), ^1H n.m.r. (119), ^{13}C n.m.r. (300)
1:2-$C_2B_9H_{13}$,NC_5H_{10}	188	
1:2-$C_2B_9H_{13}$,$2NC_5H_{10}$	187–8	^{11}B n.m.r. (168), ^1H n.m.r. (168)
1:2-$C_2HCH_3B_9H_{11}$,N_2H_4	186	
1:2-$C_2(CH_3)_2B_9H_{11}$,$N(CH_3)_3$	119	m.p. 141–3°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
1:7-$C_2B_9H_{13}$,$N(CH_3)_3$		^{13}C n.m.r. (300)
1:7-$C_2(CH_3)_2B_9H_{11}$,$N(CH_3)_3$	119	m.p. 147–8°C, i.r. (119), ^{11}B n.m.r. (119), ^1H n.m.r. (119)
1:7-$C_2(C_6H_5)_2B_9H_{11}$,N_2H_4	173	m.p. 178–9°C
1:2-$C_2B_9H_{10}(CH_2NH_2)_2^-$	189	$(C_6H_5)_3CH_3P^+$ salt: m.p. 139–40°C
1:2-$C_2B_9H_{11}(CH_2NH_2)_2$	189	m.p. 249–50°C decomp.
1:2-$C_2B_9H_{12}[CH_2N(C_2H_5)_2]$	189	m.p. 221–2°C

* $C_2B_9H_{13}$,L may also be formulated as a salt: $[LH]^+[C_2B_9H_{12}]^-$.

Table XXVI.—$C_2B_9H_{11}$, *Ligand Derivatives*

Formula	Preparation references	Properties and references
sym-(3):1:2-$C_2B_9H_{11}$,C_4H_8O	191	m.p. 153°C, i.r. (191), ^{11}B n.m.r. (191), ^1H n.m.r. (191)
asym-(3):1:2-$C_2B_9H_{11}$,C_4H_8O	191	m.p. 148°C, i.r. (191), ^{11}B n.m.r. (191), ^1H n.m.r. (191)
sym-(3):1:2-$C_2B_9H_{11}$,CH_3CN	191	m.p. 212°C, i.r. (191)
asym-(3):1:2-$C_2B_9H_{11}$,C_5H_5N	191–2	m.p. 160°C, i.r. (191)
(3):1:2-$C_2B_9H_{11}$,C_9H_7N	192	m.p. 231–2°C
sym-(3):1:2-$C_2(CH_3)_2B_9H_9$,C_4H_8O	191	m.p. 158°C, i.r. (191)
asym-(3):1:2-$C_2(CH_3)_2B_9H_9$,C_4H_8O	191	m.p. 150°C, i.r. (191)
asym-(3):1:2-$C_2(CH_3)_2B_9H_9$,$S(C_2H_5)_2$	191	m.p. 96°C, i.r. (191)
(3):1:2-$C_2(CH_3)_2B_9H_9$,CH_3CN	191	m.p. 152–7°C, i.r. (191)
(3):1:2-$C_2(CH_3)_2B_9H_9$,C_2H_5NC	111	m.p. 105–6°C, i.r. (111)
(3):1:2-$C_2(CH_3)_2B_9H_9$,$N(C_2H_5)_3$	111	m.p. 143–4°C, i.r. (111)
asym-(3):1:2-$C_2(CH_3)_2B_9H_9$,C_5H_5N	191	m.p. 158°C, i.r. (191)
(3):1:2-$C_2(C_2H_5)_2B_9H_9$,C_5H_5N	192	m.p. 166–7°C
(3):1:2-$C_2HC_6H_5B_9H_9$,$N(C_2H_5)_3$	111, 120	m.p. 156–9°C, decomp., i.r. (111)
(3):1:2-$C_2HC_6H_5B_9H_9$,C_5H_5N	192	m.p. 218–20°C
(3):1:2-$C_2HC_6H_5B_9H_9$,$P(C_6H_5)_3$	111, 120	m.p. 252°C decomp.
(3):1:2-$C_2HCH_3B_9H_8Br$,$N(CH_3)_3$ (Isomer A)	193	m.p. 152°C decomp., ^1H n.m.r. (193)
(3):1:2-$C_2HCH_3B_9H_8Br$,$N(CH_3)_3$ (Isomer B)	193	m.p. 267°C decomp., ^1H n.m.r. (193)
(3):1:2-$C_2(CH_3)_2B_9H_8Br$,$N(CH_3)_3$	193	m.p. 221°C decomp., ^1H n.m.r. (193)
[(3):1:2-$C_2B_9H_{10}$,$C_5H_5N]_2Cu$	192	
[(3):1:2-$C_2B_9H_{10}$,$C_5H_5N]Cu^-$	192	$C_5H_5NH^+$ salt: m.p. 125–7°C decomp.

*Table XXVII.—*Nido-*monocarbaborane-amine Complexes*

Formula	Preparation references	Properties and references
$CB_9H_{11},N(CH_3)_3$	127	
$CB_{10}H_{12},NH_3$	127, 197–8	m.p. >400°C, i.r. (198)
$CB_{10}H_{12},NH_2CH_3$	196	m.p. 292–3°C
$CB_{10}H_{12},NH_2C_2H_5$	195–6	m.p. 234–5°C decomp., i.r. (195), ^{1}H n.m.r. (195), m.s. (195), D_2O exchange (196)
$CB_{10}H_{12},NH_2$-*n*-C_3H_7	196, 198	m.p. 220–2°C, i.r. (198)
$CB_{10}H_{12},NH_2$-*tert*-C_4H_9	196	m.p. 237–8°C
$CB_{10}H_{12},N(CH_3)_3$	127, 196–8	m.p. 345–6°C decomp., i.r. (196, 198), ^{11}B n.m.r. (196), ^{1}H n.m.r. (196), m.s. (196)
$CB_{10}H_{12},N(CH_3)_2C_2H_5$	195–6	m.p. 310–11°C, ^{1}H n.m.r. (195)
$CB_{10}H_{12},N(CH_3)_2$-*n*-C_3H_7	196	m.p. 185–7°C
$CB_{10}H_{12},N(CH_3)_2$-*tert*-C_4H_9	196	m.p. 202–4°C
$CB_{10}H_{12},N(C_2H_5)_3$	197	m.p. 180–1°C
$CB_{10}H_{12},C_5H_5N$	197	
$CB_{10}H_{11}Cl,N(CH_3)_3$	85	i.r. (85)
$CB_{10}H_{10}Cl_2$, $N(CH_3)_2$-*n*-C_3H_7	85	m.p. 240–3°C, i.r. (85)
$CB_{10}H_{11}Br,N(CH_3)_3$	85, 197	m.p. 296–7°C, i.r. (85), ^{11}B n.m.r. (85), ^{1}H n.m.r. (85)
$CB_{10}H_{11}Br,N(CH_3)_2$-*n*-$C_3H_7$	85	m.p. 179–80°C
$CB_{10}H_{11}OH,N(CH_3)_3$	197	m.p. >390°C, i.r. (197)
$CB_{10}H_{11}OCH_3,N(CH_3)_3$	197	m.p. 198–9°C, ^{11}B n.m.r. (197), ^{1}H n.m.r. (197)

Table XXVIII.—Derivatives of Closo-1:2-*dicarbadodecaborane*(12)

(a) *C*-hydrocarbon Derivatives

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2HCH_3$	30–1, 186, 199, 240, 286, 287, 290, 308–9, 364	m.p. 220–1°C, d_4^{20} 0·914, viscosity 32·8 P at 25°C, $\Delta H_{comb.}$ 59·5 kJ mol^{-1}, μ 15·8 × 10^{-3} C m (4·75 D) (294), ^{1}H n.m.r. (290), i.r. (283, 290)
$B_{10}H_{10}C_2HC_2H_5$	199, 286–7, 308–9	m.p. 52–3°C, b.p. 75–80°C at 0·5 torr
$B_{10}H_{10}C_2H$-*n*-C_3H_7	9, 30, 199, 286, 309, 350	m.p. 68–9°C
$B_{10}H_{10}C_2H$-*iso*-C_3H_7	9, 31, 286–7, 308	m.p. −2°C, b.p. 100°C at 4 torr, n_D^{25} 1·5395, d_4^{20} 0·9665, viscosity 2·22 Ns m^{-2} (22·2 P) at 28·7°C, u.v. (31)
$B_{10}H_{10}C_2H[CH_2CH_2CH(CH_3)_2]$	9, 30	m.p. 33°C
$B_{10}H_{10}C_2H$-*n*-C_4H_9	30, 240, 286, 308	m.p. 11°C, b.p. 75°C at 0·01 torr
	9	n_D^{20} 1·5315, d_4^{20} 0·9109
$B_{10}H_{10}C_2HC_5H_{11}$	9	
$B_{10}H_{10}C_2HC_6H_{13}$	9, 30, 199	b.p. 101–2°C at 0·5 mm, n_D^{25} 1·5211
$B_{10}H_{10}C_2HC_{10}H_{21}$	9	
$B_{10}H_{10}C_2HCH{:}CH_2$	9, 30, 199, 240, 286–7, 308, 321	m.p. 79–80°C, b.p. 105°C at 5 torr, i.r. (450)
$B_{10}H_{10}C_2HCCH_3{:}CH_2$	9, 30–1, 286	m.p. 47–8°C, b.p. 60°C at 1 torr, n_D^{50} 1·5432, d_4^{25} 0·942, v.p. (31), i.r. (31), u.v. (31)
$B_{10}H_{10}C_2H{—}CH_2.CH{:}CH_2$	9, 14, 240	m.p. 63–5°C, b.p. 80–4°C at 0·4 torr
$B_{10}H_{10}C_2H{—}CH{:}CH.CH_3$	9	
$B_{10}H_{10}C_2H{—}CH_2CH_2CH{:}CH_2$	9, 186	m.p. 45–6°C, b.p. 99–101°C at 0·2 torr

Table XXVIII.—continued

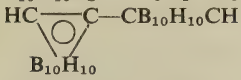
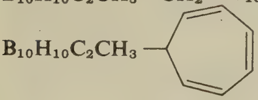
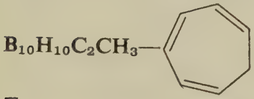
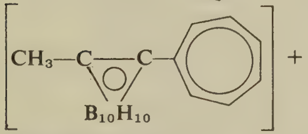
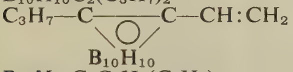
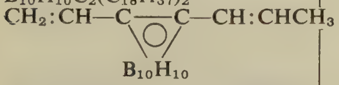
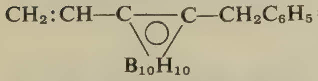
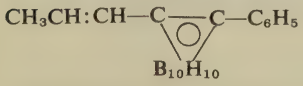
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H{-}CH_2.CCH_3{:}CH_2$	9	b.p. 87°C at 0·15 torr
$B_{10}H_{10}C_2H{-}C{\vdots}CH$	9, 200	m.p. 76–7°C
$B_{10}H_{10}C_2H{-}(CH_2)_3C{\vdots}CH$	9	b.p. 68°C at 10^{-5} torr, n_D^{20} 1·5463
$B_{10}H_{10}C_2HC_6H_5$	9, 30, 199, 267–8, 286–7, 308, 310, 384	m.p. 69–70°C, i.r. (283, 450)
$B_{10}H_{10}C_2H{-}CH_2C_6H_5$	9, 362	m.p. 52–3°C
$B_{10}H_{10}C_2H{-}(CH_2)_2C_6H_5$	322	m.p. 61–2°C
$B_{10}H_{10}C_2H{-}(CH_2)_3C_6H_5$	322	m.p. 44°C
$B_{10}H_{10}C_2H{-}C_6H_4.CH_3$-*p*	9	m.p. 152–3°C
	268	m.p. 225–6°C
$B_{10}H_{10}C_2H{-}CH_2D$	353	
$B_{10}H_{10}C_2DCH_3$	353	
$B_{10}H_{10}C_2(CH_3)_2$	9, 240, 290, 322, 351, 362–3	m.p. 265°C, i.r. (190), ^{1}H n.m.r. (190), Electron diffraction (256)
$B_{10}H_{10}C_2CH_3.C_4H_9$	287	m.p. 10–11°C, b.p. 105–6°C at 2 torr, n_D^{20} 1·5310, d_4^{20} 0·9092
$B_{10}H_{10}C_2CH_3{-}CH_2CH(CH_3)_2$	362	m.p. 100–1°C
$B_{10}H_{10}C_2CH_3{-}CH{:}CH_2$	9, 362	m.p. 120–3°C or 164–5°C
$B_{10}H_{10}C_2CH_3{-}CCH_3{:}CH_2$	9	b.p. 77–82°C at 0·3 torr
$B_{10}H_{10}C_2CH_3{-}CH_2CH{:}CH_2$	9, 186, 240, 329	m.p. 17–18°C, b.p. 77–82°C at 0·3 torr
$B_{10}H_{10}C_2CH_3{-}CH_2{-}C{\vdots}CH$	362	m.p. 92–4°C
$B_{10}H_{10}C_2CH_3.C_6H_5$	362	
$B_{10}H_{10}C_2CH_3{-}CH_2{-}C_{10}H_7$-α	362	m.p. 183–4°C
	323	m.p. 58°C, i.r. (323), u.v. (323)
	323	m.p. 93–4°C, i.r. (323), u.v. (323)
	323	Br^- salt: m.p. 103–5°C, SbF_6^- salt: m.p. >300°C, ^{1}H n.m.r. (323), u.v. (323)
$B_{10}H_{10}C_2(C_3H_7)_2$	9	
	362	m.p. 33–4°C
$B_{10}H_{10}C_2C_6H_5(C_3H_7)$	362	m.p. 96–7°C
$B_{10}H_{10}C_2[CH(CH_3)_2]_2$	199	m.p. 104–5°C
$B_{10}H_{10}C_2C_6H_5{-}C_9H_{19}$	362	m.p. 185–6°C
$B_{10}H_{10}C_2C_6H_5{-}C_{10}H_{21}$	362	m.p. 187–8°C
$B_{10}H_{10}C_2(C_{18}H_{37})_2$	9	m.p. 45°C
	362	m.p. 92–3°C
	362	m.p. 110–11°C
	362	m.p. 70–1°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2(CH_2CH{:}CH_2)_2$	9	
$B_{10}H_{10}C_2(CCH_3{:}CH_2)_2$	9, 199	m.p. 82–3°C
$B_{10}H_{10}C_2[CH{:}C(CH_3)_2]_2$	308	m.p. 80°C, b.p. 105–7°C at 1 torr
$B_{10}H_{10}C_2(C_6H_5)_2$	9, 31, 267–8, 287	m.p. 148–9°C
$B_{10}H_{10}C_2C_6H_5—CH_2C_6H_5$	362	m.p. 98–9°C
$B_{10}H_{10}C_2C_6H_5—CH_2—C_{10}H_7\text{-}\alpha$	362	m.p. 169–70°C
$B_{10}H_{10}C_2(CH_2C_6H_5)_2$	362	m.p. 151–2°C
$B_{10}H_{10}C_2(CH_2—C_{10}H_7\text{-}\alpha)_2$	362	m.p. 215–16°C

(b) *C*-halogenated Derivatives

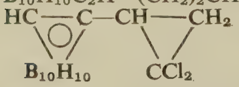
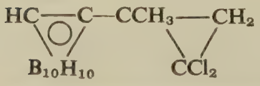
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2HCl$	359	m.p. 210–12°C, μ $10{\cdot}33 \times 10^{-30}$ C m (3·10 D) (294)
$B_{10}H_{10}C_2HBr$	380	m.p. 178–80°C, μ $11{\cdot}2\text{–}11{\cdot}5 \times 10^{-30}$ C m (3·36–3·45 D) (294)
$B_{10}H_{10}C_2HI$	186	m.p. 131–6°C
$B_{10}H_{10}C_2Cl_2$	380	m.p. 231–2°C
$B_{10}H_{10}C_2Br_2$	291	μ $9{\cdot}40 \times 10^{-30}$ C m (2·82 D) (291)
$B_{10}H_{10}C_2I_2$	379	m.p. 164–5°C
$B_{10}H_{10}C_2H—CH_2Cl$	9, 199, 286, 309	m.p. 91–2°C, ^{35}Cl n.q.r. (415, 450)
$B_{10}H_{10}C_2H—(CH_2)_2Cl$	9, 199, 286, 309	m.p. 82°C, ^{35}Cl n.q.r. (415)
$B_{10}H_{10}C_2H—(CH_2)_3Cl$	9, 309	m.p. 55°C, b.p. 104–8°C at 0·2 torr, ^{35}Cl n.q.r. (415)
$B_{10}H_{10}C_2H—(CH_2)_4Cl$	309	^{35}Cl n.q.r. (415), m.p. 38–9°C
$B_{10}H_{10}C_2H—CHCH_3Cl$	320	b.p. 105–6°C at 2 torr, n_D^{20} 1·5563
$B_{10}H_{10}C_2H—CH_2Br$	9, 30, 31, 240, 286, 290, 309	m.p. 47–9°C, b.p. 85°C at 0·3 torr, i.r. (290), ^1H n.m.r. (290)
$B_{10}H_{10}C_2H—(CH_2)_2Br$	9, 199, 286, 309	m.p. 114–15°C
$B_{10}H_{10}C_2H—(CH_2)_3Br$	309	m.p. 40–1°C
$B_{10}H_{10}C_2H—(CH_2)_4Br$	309	m.p. 55–6°C
$B_{10}H_{10}C_2H—CHCH_3—Br$	320	m.p. 29–30°C, b.p. 102°C at 2 torr, n_D^{20} 1·5760
$B_{10}H_{10}C_2H—(CH_2)_2I$	9, 286, 322	m.p. 130–1°C
$B_{10}H_{10}C_2H—(CH_2)_3I$	9, 322	m.p. 56–8°C
$B_{10}H_{10}C_2H—(CH_2)_4I$	322	m.p. 46–7°C
$B_{10}H_{10}C_2H—C\vdots CBr$	9	m.p. 123–4°C
$B_{10}H_{10}C_2H—C\vdots CI$	9	m.p. 144–5°C
$B_{10}H_{10}C_2H—CHBr.CH_2Br$	320	b.p. 139–40°C at 2 torr, n_D^{20} 1·6067
$B_{10}H_{10}C_2H—CCH_3Br.CH_2Br$	9, 344	m.p. 53°C, ^1H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H—(CH_2)_2CHOH.CH_2Cl$	9, 186	b.p. 135–45°C at 0·1 torr
	325	m.p. 73–4°C, i.r. (325), ^1H n.m.r. (325)
	325	m.p. 60–1°C, i.r. (325), ^1H n.m.r. (325)

Table XXVIII.—continued

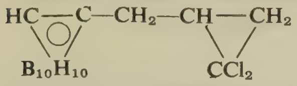
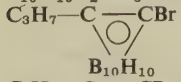
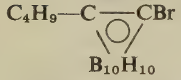
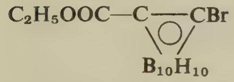
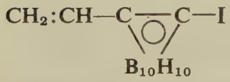
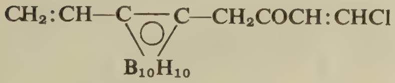
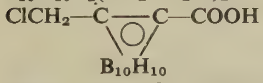
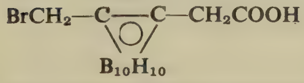
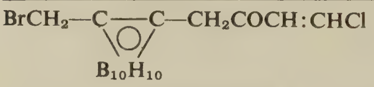
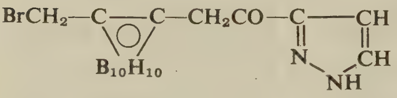
Formula	Preparation references	Properties and references
 $\underset{B_{10}H_{10}}{HC—C}—CH_2—\underset{CCl_2}{CH—CH_2}$	325	m.p. 58–9°C, i.r. (325), ^1H n.m.r. (325)
$B_{10}H_{10}C_2H—CH_2COCH:CHCl$	338	m.p. 49–50°C
$B_{10}H_{10}C_2H—C_6H_4F$-*p*	9, 281, 310	m.p. 140–1°C, ^{19}F n.m.r. (281, 310)
$B_{10}H_{10}C_2H—C_6H_4F$-*m*	9, 281, 310	m.p. 68–9°C, ^{35}Cl n.q.r. (281, 310)
$B_{10}H_{10}C_2H—C_6H_4Cl$-*p*	176, 262, 324	m.p. 143–5°C, ^{19}F n.m.r. (415, 450)
$B_{10}H_{10}C_2H—C_6H_4Cl$-*m*	176	m.p. 97–9°C, ^{35}Cl n.q.r. (416)
$B_{10}H_{10}C_2H—C_6H_4Br$-*p*	9, 174, 262, 286, 310, 324	m.p. 135–6°C, ^{79}Br n.q.r. (415)
$B_{10}H_{10}C_2H—C_6H_4Br$-*m*	9, 310	m.p. 107–8°C
$B_{10}H_{10}C_2H—C_6H_4I$-*p*	176, 324	m.p. 112–13°C
$B_{10}H_{10}C_2CH_3.Cl$	359	m.p. 235–6°C, μ 11·9–12·2 $\times 10^{-30}$ C m (3·57–3·65 D) (294)
$B_{10}H_{10}C_2CH_3.Br$	9, 358, 374, 379	m.p. 222–4°C, μ 12·4–12·6 $\times 10^{-30}$ C m (3·72–3·78 D) (294)
$B_{10}H_{10}C_2CH_3.I$	9	m.p. 126–7°C
$B_{10}H_{10}C_2CH_3—CH_2Br$	9, 199, 349, 350, 353	m.p. 125–7°C, b.p. 110°C at 0·3 torr
$B_{10}H_{10}C_2CH_3—COCH_2Br$	9, 337	m.p. 61°C, i.r. (337), ^1H n.m.r. (337)
$B_{10}H_{10}C_2CH_3—CHBr.COC_6H_5$	337	m.p. 89–90°C
$B_{10}H_{10}C_2CH_3—CH_2COCH:CHCl$	338	m.p. 79–80°C
$B_{10}H_{10}C_2CH_3—C_6H_4F$-*p*	281	m.p. 84–5°C, ^{19}F n.m.r. (281)
$B_{10}H_{10}C_2CH_3—C_6H_4F$-*m*	281	m.p. 70–1°C, ^{19}F n.m.r.(281)
 $C_3H_7—\underset{B_{10}H_{10}}{C—CBr}$	9, 30	m.p. 44–5°C, b.p. 107°C at 1 torr
 $C_4H_9—\underset{B_{10}H_{10}}{C—CBr}$	9, 30	b.p. 85–90°C at 0·5 torr, n_D^{23} 1·5500
 $C_2H_5OOC—\underset{B_{10}H_{10}}{C—CBr}$	9	
 $CH_2:CH—\underset{B_{10}H_{10}}{C—C}—I$	379	m.p. 124–6°C
 $CH_2:CH—\underset{B_{10}H_{10}}{C—C}—CH_2COCH:CHCl$	338	m.p. 79–80°C
$B_{10}H_{10}C_2(CH_2Cl)_2$	9, 30, 199, 286, 309	m.p. 119–20°C, ^{35}Cl n.q.r. (415, 450)
$B_{10}H_{10}C_2(CH_2Br)_2$	9, 31, 286, 309	m.p. 68–70°C, ^{79}Br n.q.r. (415), *X*-ray (245–7)
$B_{10}H_{10}C_2(CH_2CH_2Cl)_2$	9	m.p. 157–8°C
 $ClCH_2—\underset{B_{10}H_{10}}{C—C}—COOH$	375	m.p. 124–6°C
 $BrCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2COOH$	338	m.p. 144–5°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	338	m.p. 36–7°C
	338	m.p. 144–5°C
$B_{10}H_{10}C_2C_6H_5Cl$	332, 378–9	m.p. 53–4°C, ^{35}Cl n.q.r. (416)
$B_{10}H_{10}C_2C_6H_5Br$	378	m.p. 76–7°C
$B_{10}H_{10}C_2C_6H_5I$	378, 379	m.p. 96–7°C
$B_{10}H_{10}C_2C_6H_5{-}(CH_2)_3Cl$	349, 350	m.p. 88–9°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2CHOH.CH_2Cl$	335	m.p. 72–4°C, i.r. (335)
$B_{10}H_{10}C_2C_6H_5{-}CH_2COCH_2Cl$	335	m.p. 92–4°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2COCH_2Br$	337	m.p. 93–4°C

(c) Side-chain Ether and Epoxide Derivatives

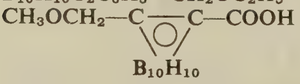
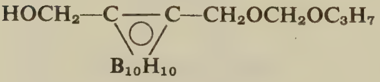
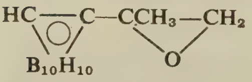
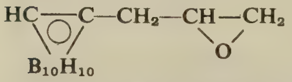
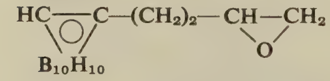
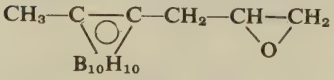
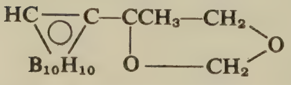
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2HOC_2H_5$	9, 311	m.p. −22°C, b.p. 70°C at 0·1 torr, n_D^{27} 1·5445, i.r. (311), ^{11}B n.m.r. (311)
$B_{10}H_{10}C_2H{-}CH(OC_2H_5)_2$	327	
$B_{10}H_{10}C_2H{-}CCH_3{:}COH.OCH_3$	9	b.p. 95–100°C at 0·5 torr
$B_{10}H_{10}C_2H{-}CH_2OCHCH_3.OC_4H_9$	322	m.p. 56–7°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2OC_2H_5$	286	m.p. 59–60°C
	377	m.p. 96–8°C, pK_a 2·33
	326	i.r. (326)
	9, 31	b.p. 96–100°C at 0·3 torr, n_D^{25} 1·5483
	9, 240	m.p. 67–8°C
	9, 186	m.p. 60–2°C, b.p. 132–5°C at 0·4 torr
	335, 371	m.p. 51–2°C
	326	m.p. 36–8°C, i.r. (326)

Table XXVIII.—continued

(d) *C*-substituted Alcohol and Phenol Derivatives

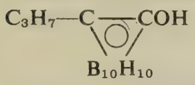
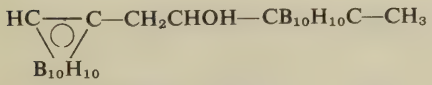
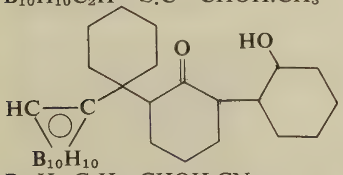
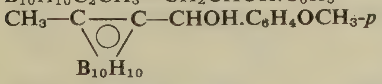
Formula	Preparation references	Properties and references
 $C_3H_7—C—COH$ ($B_{10}H_{10}$)	9	
$B_{10}H_{10}C_2H—CH_2OH$	9, 199, 240, 286, 288, 309, 331	m.p. 229–30°C
$B_{10}H_{10}C_2H—(CH_2)_2OH$	9, 286, 309, 335	m.p. 51–2°C
$B_{10}H_{10}C_2H—(CH_2)_3OH$	9, 309	m.p. 53–4°C
$B_{10}H_{10}C_2H—(CH_2)_4OH$	309	m.p. 46–8°C
$B_{10}H_{10}C_2H—CHCH_3OH$	9	
$B_{10}H_{10}C_2H—CHC_2H_5OH$	331	m.p. 43–5°C
$B_{10}H_{10}C_2H—CHOH.C_4H_9$	331	m.p. 31°C
$B_{10}H_{10}C_2H—CHOH.C_6H_5$	9, 331	m.p. 67–9°C
$B_{10}H_{10}C_2H—CH_2CHOH.CH_3$	322, 335	m.p. 77–8°C
$B_{10}H_{10}C_2H—CH_2C(CH_3)_2OH$	9	b.p. 92–6°C at 3×10^{-4} torr, n_D^{20} 1·5478
 $HC—C—CH_2CHOH—CB_{10}H_{10}C—CH_3$ ($B_{10}H_{10}$)	329	m.p. 239–40°C
$B_{10}H_{10}C_2H—C\vdots C—CH_2OH$	9	m.p. 87–8°C
$B_{10}H_{10}C_2H—C\vdots C—CHOH.CH_3$	9	m.p. 77–8°C
	341	m.p. 72–3°C
$B_{10}H_{10}C_2H—CHOH.CN$	327	m.p. 99–100°C
$B_{10}H_{10}C_2H—CCH_3OH.CH_2NO_2$	344	m.p. 103°C, ^1H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H—CH_2CHOH.CH_2OOCH$	9	m.p. 50–60°C
$B_{10}H_{10}C_2H—CH_2CH_2CHOH.CH_2Cl$	9, 186	b.p. 135–45°C at 0·1 torr
$B_{10}H_{10}C_2H—CH_2CH_2CHCH_2OH.OOCCF_3$	186	b.p. 148–50°C at 0·1 torr
$B_{10}H_{10}C_2H—CCH_3{:}COH.OCH_3$	9	b.p. 95–100°C at 0·5 torr
$B_{10}H_{10}C_2H—CCH_3OH.CH_2OH$	326	m.p. 91–3°C, i.r. (326)
$B_{10}H_{10}C_2H—CH_2CHOH.CH_2OH$ (isomer a)	9, 240	m.p. 89–90°C
$B_{10}H_{10}C_2H—CH_2CHOH.CH_2OH$ (isomer b)	9, 240	m.p. 92–3°C
$B_{10}H_{10}C_2CH_3—CH_2OH$	329, 370	m.p. 268–9°C
$B_{10}H_{10}C_2CH_3—CH_2CH_2OH$	335	m.p. 59–60°C
$B_{10}H_{10}C_2CH_3—CHCH_3.OH$	9, 328–9, 341, 370	m.p. 159°C
$B_{10}H_{10}C_2CH_3—C(CH_3)_2OH$	329, 336	m.p. 87–9°C, ^1H n.m.r. (329)
$B_{10}H_{10}C_2CH_3—CHOH.CH{:}CH_2$	370	m.p. 45–6°C
$B_{10}H_{10}C_2CH_3—CHOH.CH{:}CHCH_3$	370	m.p. 55–6°C
$B_{10}H_{10}C_2CH_3—CHOH.C_6H_5$	9, 330, 341, 368–71	m.p. 107–8°C, 120°C
$B_{10}H_{10}C_2CH_3—CH_2CHOH.CH_3$	335	m.p. 52–4°C
$B_{10}H_{10}C_2CH_3—CH_2CHOH.C_6H_5$	335	m.p. 92–3°C, i.r. (335)
 $CH_3—C—C—CHOH.C_6H_4OCH_3$-*p* ($B_{10}H_{10}$)	370	m.p. 126–7°C

Table XXVIII.—continued

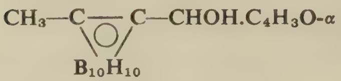
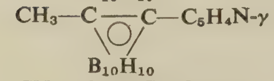
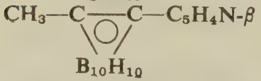
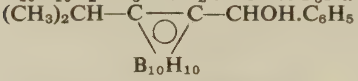
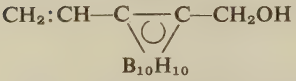
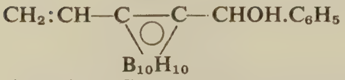
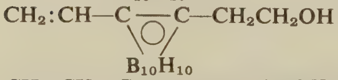
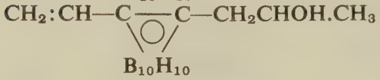
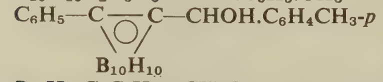
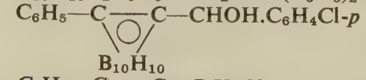
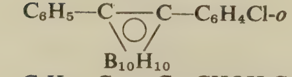
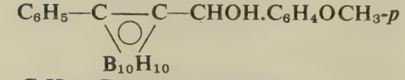
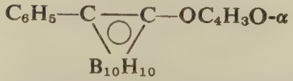
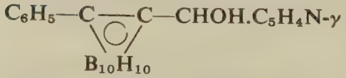
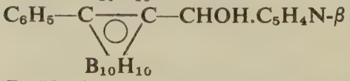
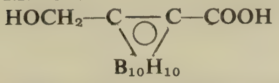
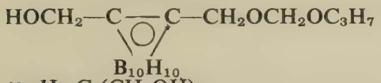
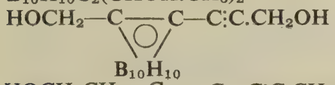
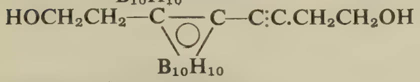
Formula	Preparation references	Properties and references
 $CH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_4H_3O\text{-}\alpha$	370	b.p. 135–6°C at 1·0 torr
 $CH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}C_5H_4N\text{-}\gamma$	370	m.p. 241–2°C
 $CH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}C_5H_4N\text{-}\beta$	370	m.p. 224–5°C
$B_{10}H_{10}C_2CH_3{-}CH_2CHOH.SO_3Na$	327	m.p. 168–70°C
 $(CH_3)_2CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_6H_5$	368	m.p. 149–50°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2OH$	370	m.p. 185–6°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_6H_5$	370	m.p. 107–9°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2CH_2OH$	335	m.p. 40–2°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2CHOH.CH_3$	335	b.p. 110–12°C at 1·0 torr, n_D^{20} 1·5540
$B_{10}H_{10}C_2C_6H_5{-}CH_2OH$	370	m.p. 89–90°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2CH_2OH$	286, 335, 350	m.p. 82–4°C
$B_{10}H_{10}C_2C_6H_5{-}CHOH.CH_3$	328	m.p. 99–100°C
$B_{10}H_{10}C_2C_6H_5{-}CHOH.CH{:}CH_2$	370	m.p. 63–4°C
$B_{10}H_{10}C_2C_6H_5{-}CHOH.CH{:}CHCH_3$	370	m.p. 82–3°C
$B_{10}H_{10}C_2C_6H_5{-}CHOH.C_6H_5$	317, 321, 329, 368–70	m.p. 122–4°C
$B_{10}H_{10}C_2C_6H_5{-}COH.C_6H_5.CH_3$	329	m.p. 128–9°C, ^{1}H n.m.r. (329)
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_6H_4CH_3\text{-}p$	321	m.p. 78–9°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2CHOH.CH_3$	335	m.p. 68–9°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2COH(C_6H_5)_2$	328	m.p. 154–5°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_6H_4Cl\text{-}p$	341, 369	m.p. 156–7°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}C_6H_4Cl\text{-}o$	370	m.p. 152–3°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_6H_4OCH_3\text{-}p$	370	m.p. 138–9°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}OC_4H_3O\text{-}\alpha$	370	m.p. 113–14°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_5H_4N\text{-}\gamma$	370	m.p. 194–5°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CHOH.C_5H_4N\text{-}\beta$	370	m.p. 228–9°C
$B_{10}H_{10}C_2C_6H_5{-}CH_2CHOH.CH_2Cl$	335	m.p. 72–4°C, i.r. (335)

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $HOCH_2-\underbrace{C-C}_{B_{10}H_{10}}-COOH$	257	
 $HOCH_2-\underbrace{C-C}_{B_{10}H_{10}}-CH_2OCH_2OC_3H_7$	326	i.r. (326)
$B_{10}H_{10}C_2(CH_2OH)_2$	199, 201, 214, 240, 286, 309, 350	m.p. 303–4°C, pK_a 12·12 (201)
$B_{10}H_{10}C_2(CH_2CH_2OH)_2$	9, 186, 240, 286	m.p. 124–5°C
$B_{10}H_{10}C_2(CHOH.CH_3)_2$	9, 240	m.p. >400°C
 $HOCH_2-\underbrace{C-C}_{B_{10}H_{10}}-C\vdots C.CH_2OH$	9, 199	m.p. 163–4°C
 $HOCH_2CH_2-\underbrace{C-C}_{B_{10}H_{10}}-C\vdots C.CH_2CH_2OH$	9	m.p. 101–2°C
$B_{10}H_{10}C_2(CHOHC_6H_5)_2$	370	m.p. 134–5°C

(e) *C*-substituted Aldehyde and Ketone Derivatives

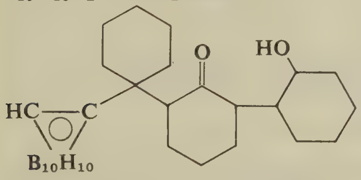
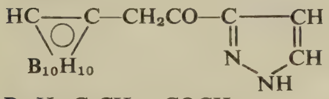
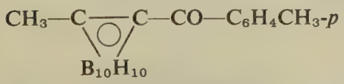
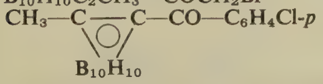
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H—CHO$	329–31, 333	m.p. 212–13°C, i.r. (329)
$B_{10}H_{10}C_2H—CH_2CHO$	329, 331	m.p. 94–5°C
$B_{10}H_{10}C_2CH_3—CHO$	329–30	m.p. 222–3°C
$B_{10}H_{10}C_2CH_3—CH_2CHO$	329	m.p. 140–2°C
$B_{10}H_{10}C_2C_6H_5—CHO$	332	m.p. 57–8°C
$B_{10}H_{10}C_2H—COCH_3$	328	m.p. 54–5°C
$B_{10}H_{10}C_2H—COC_6H_5$	9, 328, 334	m.p. 57–8°C, i.r. (334)
$B_{10}H_{10}C_2H—CH_2COCH_3$	9	m.p. 167–9°C
$B_{10}H_{10}C_2H—CH_2COC_6H_5$	334	m.p. 52–3°C, i.r. (334)
$B_{10}H_{10}C_2H—CH_2COCH{:}CHCl$	338	m.p. 49–50°C
	341	m.p. 72–3°C
	338	m.p. 130–1°C
$B_{10}H_{10}C_2CH_3—COCH_3$	9, 328, 336, 341	m.p. 118–19°C, i.r. (337), ^{1}H n.m.r. (337), polarography (337)
$B_{10}H_{10}C_2CH_3—COC_6H_5$	9, 334, 337, 369, 372	m.p. 66–7°C, i.r. (334), polarography (337)
 $CH_3-\underbrace{C-C}_{B_{10}H_{10}}-CO-C_6H_4CH_3\text{-}p$	372	m.p. 101–2°C
$B_{10}H_{10}C_2CH_3—COCH_2Br$	9, 337	m.p. 61°C
 $CH_3-\underbrace{C-C}_{B_{10}H_{10}}-CO-C_6H_4Cl\text{-}p$	372	m.p. 127°C

Table XXVIII.—continued

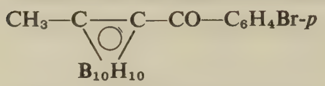
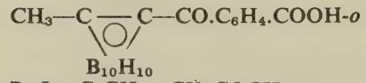
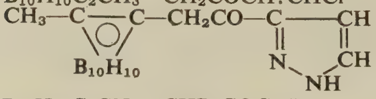
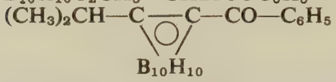
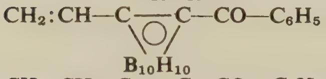
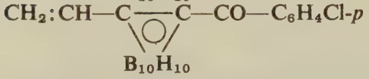
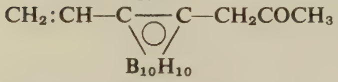
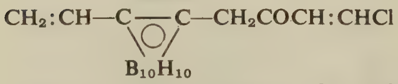
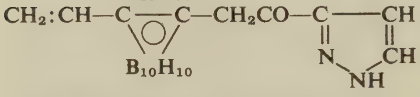
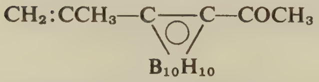
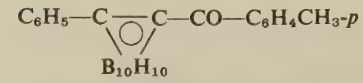
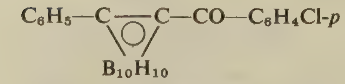
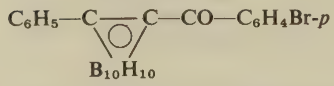
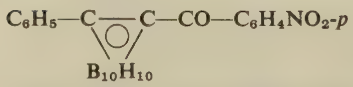
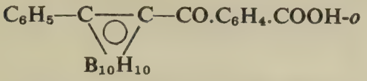
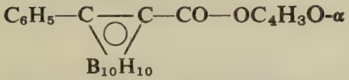
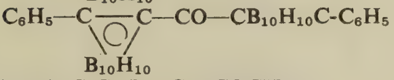
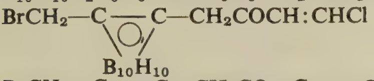
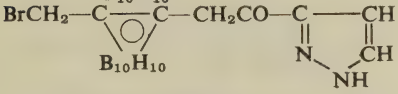
Formula	Preparation references	Properties and references
 $CH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4Br\text{-}p$	341	m.p. 112–13°C
 $CH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO.C_6H_4.COOH\text{-}o$	341	m.p. 242–4°C
$B_{10}H_{10}C_2CH_3{-}CH_2COCH_3$	335	m.p. 33–4°C, i.r. (335)
$B_{10}H_{10}C_2CH_3{-}CH_2COC_6H_5$	335	m.p. 72–3°C, i.r. (335)
$B_{10}H_{10}C_2CH_3{-}CH_2COCH{:}CHCl$	338	m.p. 36–7°C
	338	m.p. 164–5°C
$B_{10}H_{10}C_2CH_3{-}CHBrCOC_6H_5$	337	m.p. 89–90°C
 $(CH_3)_2CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_5$	334	m.p. 44–5°C, i.r. (334)
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_5$	372	m.p. 40–1°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4Cl\text{-}p$	372	m.p. 80°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2COCH_3$	335	m.p. 36–7°C
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2COCH{:}CHCl$	338	m.p. 79–80°C
	338	m.p. 197–8°C
 $CH_2{:}CCH_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}COCH_3$	9	m.p. 70–1°C
$B_{10}H_{10}C_2C_6H_5{-}COCH_3$	279, 286, 317, 328, 341, 372	m.p. 68–9°C
$B_{10}H_{10}C_2C_6H_5{-}COCH(CH_3)_2$	279, 317, 372	m.p. 46–7°C, b.p. 169–70°C at 2 torr
$B_{10}H_{10}C_2C_6H_5{-}COC_6H_5$	279, 317, 322, 329, 334, 369, 372	m.p. 86–7°C, i.r. (334)
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4CH_3\text{-}p$	341, 369, 372	m.p. 82–3°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4Cl\text{-}p$	341, 369, 372	m.p. 118–19°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4Br\text{-}p$	341, 369	m.p. 132–3°C
 $C_6H_5{-}\underset{B_{10}H_{10}}{C{-}C}{-}CO{-}C_6H_4NO_2\text{-}p$	372	m.p. 146–7°C
$B_{10}H_{10}C_2C_6H_5{-}COCH_2CH_2COOH$	341	m.p. 136–7°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CO.C_6H_4.COOH\text{-}o$	341	m.p. 207–8°C
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CO-OC_4H_3O\text{-}\alpha$	372	m.p. 128–9°C
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CO-CB_{10}H_{10}C\text{-}C_6H_5$	279, 317, 373	m.p. 217–18°C
$B_{10}H_{10}C_2C_6H_5-CH_2COCH_3$	328, 335	m.p. 82–3 or 147–8°C
$B_{10}H_{10}C_2C_6H_5-CH_2COCH_2Cl$	335	m.p. 92–4°C
$B_{10}H_{10}C_2C_6H_5-CH_2COCH_2Br$	337	m.p. 93–4°C
$B_{10}H_{10}C_2C_6H_5-CH_2CH_2COC_6H_5$	328	m.p. 134–5°C
$B_{10}H_{10}C_2C_6H_5-CHC_6H_5.CH_2COC(CH_3)_3$	340–1	m.p. 137–8°C
$B_{10}H_{10}C_2C_6H_5-CHC_6H_5.CH_2COC_6H_5$	340–1, 354	m.p. 150–1°C
 $BrCH_2-\underset{B_{10}H_{10}}{C-C}-CH_2COCH{:}CHCl$	338	m.p. 36–7°C
	338	m.p. 144–5°C

(f) *C*-substituted Carboxylic Acid Derivatives

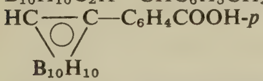
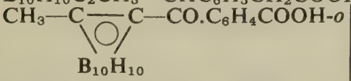
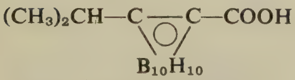
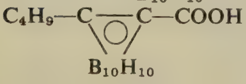
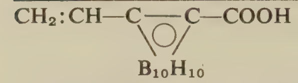
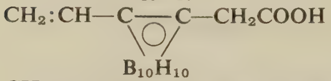
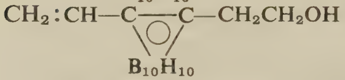
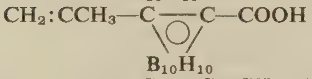
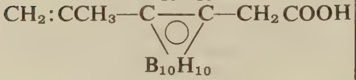
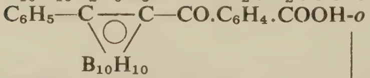
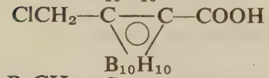
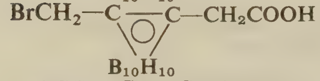
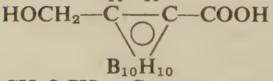
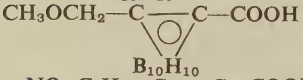
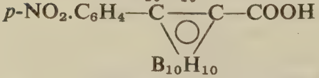
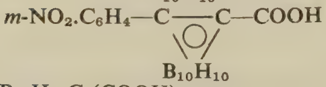
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H-COOH$	9, 240, 286, 312, 327, 342, 347, 367, 377	m.p. 151–2°C, i.r. (312, 342), pK_a 2·49
$B_{10}H_{10}C_2H-CH_2COOH$	9, 248, 286, 312, 338, 374, 377	m.p. 193–4°C, i.r. (312), pK_a 4·06
$B_{10}H_{10}C_2H-CH_2CH_2COOH$	312, 377	m.p. 158–9°C, i.r. (312)
$B_{10}H_{10}C_2H-{}^{14}COOH$	339	m.p. 150–1°C
$B_{10}H_{10}C_2H-CH_2{}^{14}COOH$	339	m.p. 191–3°C, i.r. (339)
$B_{10}H_{10}C_2H-(CH_2)_2{}^{14}COOH$	339	m.p. 146–8°C
$B_{10}H_{10}C_2H-(CH_2)_3{}^{14}COOH$	339	m.p. 157–8°C
$B_{10}H_{10}C_2H-(CH_2)_4{}^{14}COOH$	339	m.p. 153–4°C, i.r. (339)
$B_{10}H_{10}C_2H-CH_2CH(COOH)_2$	1	m.p. 146–7°C
$B_{10}H_{10}C_2H-CHC_6H_5CH_2COOH$	340	m.p. 217–18°C
 $HC-\underset{B_{10}H_{10}}{}-C-C_6H_4COOH\text{-}p$	9, 310	m.p. 274–5°C, pK_a 5·86
$B_{10}H_{10}C_2H-CCH_3(COOH)_2$	186	m.p. 146–7°C
$B_{10}H_{10}C_2H-CH_2CCH_3(COOH)_2$	9	m.p. 146–7°C
$B_{10}H_{10}C_2CH_3-COOH$	9, 81, 186, 248, 347, 374	m.p. 201–3°C, pK_a 2·53
$B_{10}H_{10}C_2CH_3-{}^{14}COOH$	339	m.p. 193–5°C
$B_{10}H_{10}C_2CH_3-CH_2COOH$	335, 338	m.p. 123–4°C
$B_{10}H_{10}C_2CH_3-(CH_2)_2COOH$	338	m.p. 164–5°C
$B_{10}H_{10}C_2CH_3-CHC_6H_5CH_2COOH$	341	
 $CH_3-\underset{B_{10}H_{10}}{C-C}-CO.C_6H_4COOH\text{-}o$	341	m.p. 242–4°C
 $(CH_3)_2CH-\underset{B_{10}H_{10}}{C-C}-COOH$	347, 377	m.p. 161–2°C, pK_a 2·56
 $C_4H_9-\underset{B_{10}H_{10}}{C-C}-COOH$	347, 377	m.p. 88–9°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $CH_2{:}CH\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	347, 377	m.p. 142–3°C, pK_a 2·72
 $CH_2{:}CH\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}CH_2COOH$	335, 338	m.p. 151–2 or 188°C
 $CH_2{:}CH\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}CH_2CH_2OH$	338	m.p. 149–51°C
 $CH_2{:}CCH_3\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	9, 240	m.p. 175°C
 $CH_2{:}CCH_3\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}CH_2COOH$	338	m.p. 172–3°C
$B_{10}H_{10}C_2C_6H_5\text{—}COOH$	9, 312, 321, 347, 377	m.p. 143–4°C, pK_a 3·12
$B_{10}H_{10}C_2C_6H_5\text{—}CH_2COOH$	338, 366	m.p. 196–8°C
$B_{10}H_{10}C_2C_6H_5\text{—}(CH_2)_2COOH$	328	m.p. 155–7°C
$B_{10}H_{10}C_2C_6H_5\text{—}COCH_2CH_2COOH$	341	m.p. 136–7°C
 $C_6H_5\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}CO.C_6H_4.COOH\text{-}o$	341	m.p. 207–8°C
 $ClCH_2\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	374–5	m.p. 127°C
 $BrCH_2\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}CH_2COOH$	338	m.p. 144–5°C
 $HOCH_2\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	257	
 $CH_3OCH_2\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	377	m.p. 96–8°C, pK_a 2·33
 $p\text{-}NO_2.C_6H_4\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	174	
 $m\text{-}NO_2.C_6H_4\text{—}\underset{B_{10}H_{10}}{C\text{—}C}\text{—}COOH$	174	
$B_{10}H_{10}C_2(COOH)_2$	9, 186, 240, 347	m.p. 232°C
$B_{10}H_{10}C_2(CH_2COOH)_2$	9, 240	m.p. 203–5°C

(g) *C*-substituted Ester Derivatives

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H\text{—}COOCH_3$	9, 30, 342	m.p. 73°C
$B_{10}H_{10}C_2H\text{—}COOC_2H_5$	286, 312, 316, 334	m.p. 62–3°C, i.r. (334)
$B_{10}H_{10}C_2H\text{—}CH_2COOCH_3$	9	m.p. 39–40°C
$B_{10}H_{10}C_2H\text{—}CH_2COOC_2H_5$	312	b.p. 93–4°C at 1·0 torr, n_D^{20} 1·5182
$B_{10}H_{10}C_2H\text{—}(CH_2)_3COOC_2H_5$	312	m.p. 31–2°C
$B_{10}H_{10}C_2H\text{—}C{\vdots}C\text{—}COOCH_3$	9	m.p. 56–7°C

Table XXVIII.—*continued*

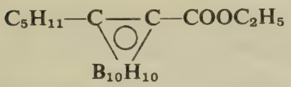
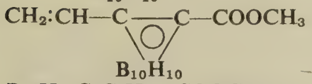
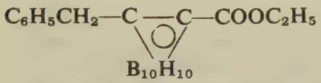
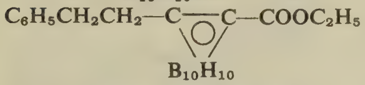
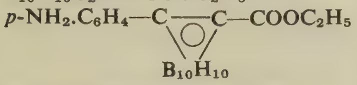
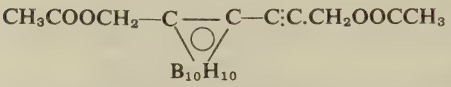
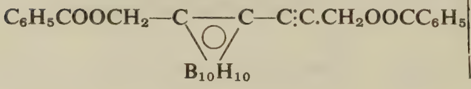
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H\text{—}CH_2CH(COOC_2H_5)_2$	9, 199	b.p. 144–8°C at 0·2 torr
$B_{10}H_{10}C_2H\text{—}CH_2CCH_3(COOC_2H_5)_2$	9, 199	m.p. 36°C, b.p. 164°C at 0·5 torr, n_D^{25} 1·5131
$B_{10}H_{10}C_2CH_3\text{—}COOC_2H_5$	334	m.p. 7–9°C, b.p. 101–3°C at 2–3 torr, n_D^{20} 1·5197, d_4^{20} 1·0003, i.r. (334)
 $C_5H_{11}\text{—}\underbrace{C\text{—}C}_{B_{10}H_{10}}\text{—}COOC_2H_5$	312	b.p. 160–1°C at 3 torr, n_D^{20} 1·5129, d_4^{20} 0·9625
 $CH_2{:}CH\text{—}\underbrace{C\text{—}C}_{B_{10}H_{10}}\text{—}COOCH_3$	321	m.p. 42–3°C
$B_{10}H_{10}C_2C_6H_5\text{—}COOCH_3$	9, 321	m.p. 87–8°C
$B_{10}H_{10}C_2C_6H_5\text{—}COOC_2H_5$	312, 334	m.p. 34–5°C, i.r. (334)
$B_{10}H_{10}C_2C_6H_5CH_2COOC_2H_5$	334	m.p. 10–11°C, b.p. 110–12°C at 2–3 torr, n_D^{20} 1·5276, d_4^{20} 1·0202, i.r. (334)
 $C_6H_5CH_2\text{—}\underbrace{C\text{—}C}_{B_{10}H_{10}}\text{—}COOC_2H_5$	312	m.p. 27–8°C
 $C_6H_5CH_2CH_2\text{—}\underbrace{C\text{—}C}_{B_{10}H_{10}}\text{—}COOC_2H_5$	312	b.p. 166–7°C at 1 torr, n_D^{20} 1·5582, d_4^{20} 1·0410
$B_{10}H_{10}C_2Br\text{—}COOC_2H_5$	9	
 $p\text{-}NH_2.C_6H_4\text{—}\underbrace{C\text{—}C}_{B_{10}H_{10}}\text{—}COOC_2H_5$	312	m.p. 101–2°C
$B_{10}H_{10}C_2(COOCH_3)_2$	9, 30, 199	m.p. 67–8°C, b.p. 108°C at 0·5 torr
$B_{10}H_{10}C_2(COOC_2H_5)_2$	343	m.p. 10–11°C
$B_{10}H_{10}C_2(CH_2COOCH_3)_2$	9, 31, 214, 240	m.p. 47–8°C, b.p. 151–6°C at 0·7 torr
$B_{10}H_{10}C_2(CH_2COOC_2H_5)_2$	240	m.p. 40°C
$B_{10}H_{10}C_2HCH_2OOCCH_3$	9, 30, 199, 286, 289, 309	m.p. 47–8°C, b.p. 120°C at 1 torr
$B_{10}H_{10}C_2H\text{—}CH_2OOCCH{:}CH_2$	9, 199	m.p. 17–18°C, b.p. 98–100°C at 0·2 torr, n_D^{25} 1·5390
$B_{10}H_{10}C_2H\text{—}CH_2OOC_6H_5$	322, 331	m.p. 95°C
$B_{10}H_{10}C_2H\text{—}CH_2OOCCF_3$	9, 309	m.p. 10°C, b.p. 93–4°C at 5 torr, d_4^{20} 1·1809, n_D^{20} 1·4879
$B_{10}H_{10}C_2H\text{—}CH_2CH_2OOCCH_3$	9, 30, 309	m.p. 63–4°C, b.p. 146°C at 1·6 torr
$B_{10}H_{10}C_2H\text{—}(CH_2)_3OOCCH_3$	9, 309	m.p. 31–2°C, n_D^{20} 1·5283
$B_{10}H_{10}C_2H\text{—}(CH_2)_4OOCC_6H_5$	309	m.p. 83–4°C
$B_{10}H_{10}C_2H\text{—}CHCH_3OOCCH_3$	9, 30	b.p. 85–95°C at 0·2 torr, n_D^{21} 1·5291
$B_{10}H_{10}C_2H\text{—}CHCH_3OOCC_6H_5$	331	m.p. 72–3°C
$B_{10}H_{10}C_2H\text{—}CHC_2H_5.OOCC_6H_5$	331	m.p. 63–4°C
$B_{10}H_{10}C_2H\text{—}CH_2CHCH_3.OOCCH_3$	322	m.p. 75–6°C
$B_{10}H_{10}C_2H\text{—}CH_2CHOH.CH_2OOCH$	9	m.p. 50–60°C
$B_{10}H_{10}C_2H\text{—}CH_2CH_2CHCH_2OH.OOCCF_3$	186	b.p. 148–50°C at 0·1 torr
$B_{10}H_{10}C_2H\text{—}CCH_3.CH_2NO_2.OOCCH_3$	344	m.p. 83–4°C, ^1H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H\text{—}CH(OOCCH_3)_2$	9, 321	m.p. 76–7°C
$B_{10}H_{10}C_2H\text{—}CH_2CH(CH_2OOCCH_3)_2$	199	b.p. 180–4°C at 0·3 torr
$B_{10}H_{10}C_2CH_3\text{—}CH_2OOCC_6H_5$	322	95°C
$B_{10}H_{10}C_2CH_3\text{—}CHOOCCH_3.C{:}C.CH_3$	9	liquid
$B_{10}H_{10}C_2(CH_2OOCCH_3)_2$	30, 289	m.p. 43–4°C, b.p. 100–1°C at 0·06 torr, i.r. (289), ^1H n.m.r. (289)

Table XXVIII.—continued

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2(CH_2OOCCF_3)_2$	309	m.p. 14°C, b.p. 120–30°C at 1 torr, n_D^{20} 1·4565, d_4^{20} 1·4216
 $CH_3COOCH_2-\underset{B_{10}H_{10}}{C-C}-C{:}C.CH_2OOCCH_3$	199	
 $C_6H_5COOCH_2-\underset{B_{10}H_{10}}{C-C}-C{:}C.CH_2OOCC_6H_5$	9, 199	m.p. 250°C

(h) *C*-substituted Amide and Other Carboxylic Acid Derivatives

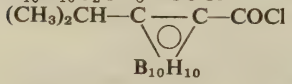
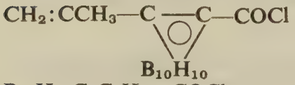
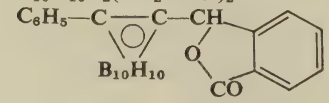
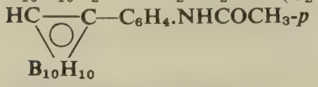
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2HCOO^-$	9, 342	$CH_3.C_5H_5N^+$ salt: m.p. 113–14°C, Ba^{2+} salt: m.p. >300°C
$B_{10}H_{10}C_2(COO)_2^{2-}$	9	NH_4^+ salt: m.p. 180–5°C decomp., $NH_2(C_2H_5)_2^+$ salt: m.p. 173–5°C, $C_5H_6N^+$ salt: m.p. 133°C
$B_{10}H_{10}C_2(CH_2COO)_2^{2-}$	9	NH_4^+ salt
$B_{10}H_{10}C_2H-COCl$	9, 240, 286, 312, 334	m.p. 39–41°C or 70°C
$B_{10}H_{10}C_2H-CH_2COCl$	312	m.p. 39°C
$B_{10}H_{10}C_2H-CH_2CH_2COCl$	312	b.p. 142–3°C at 1 torr, n_D^{20} 1·5610, d_4^{20} 1·1096
$B_{10}H_{10}C_2CH_3-COCl$	9, 334	m.p. 125–7°C
 $(CH_3)_2CH-\underset{B_{10}H_{10}}{C-C}-COCl$	334	
 $CH_2{:}CCH_3-\underset{B_{10}H_{10}}{C-C}-COCl$	9	
$B_{10}H_{10}C_2C_6H_5-COCl$	334	
$B_{10}H_{10}C_2C_6H_5-CH_2COCl$	334	
$B_{10}H_{10}C_2(COCl)_2$	9, 240	m.p. 69–70°C, b.p. 90–100°C at 2 torr
$B_{10}H_{10}C_2(CH_2COCl)_2$	9, 240	
	341, 369	m.p. 203–5°C
$B_{10}H_{10}C_2H-CONH_2$	286, 322, 334	m.p. 114–16°C, i.r. (334)
$B_{10}H_{10}C_2H-CON(C_2H_5)_2$	322, 343	m.p. 109–10°C
$B_{10}H_{10}C_2H-CONHC_6H_5$	9, 240	m.p. 132–3°C
$B_{10}H_{10}C_2H-CH_2CONH_2$	322, 334	m.p. 149–50°C, i.r. (334)
$B_{10}H_{10}C_2H-CH_2CON(C_2H_5)_2$	322, 343	m.p. 82–3°C
$B_{10}H_{10}C_2H-CH_2CH_2CONH_2$	322	m.p. 90–1°C
$B_{10}H_{10}C_2H-CH_2CH_2CON(C_2H_5)_2$	322	m.p. 46–8°C
 $\underset{B_{10}H_{10}}{HC-C}-C_6H_4.NHCOCH_3\text{-}p$	174, 324	m.p. 176–7°C
$B_{10}H_{10}C_2CH_3-CONH_2$	334	m.p. 217–18°C, i.r. (334)
$B_{10}H_{10}C_2CH_3-CONHC_6H_5$	341, 379	m.p. 143–4°C
$B_{10}H_{10}C_2CH_3-NHCOCH_3$	9	m.p. 195–7°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2C_6H_5$—$CONHC_6H_5$	341	m.p. 154–5°C
$B_{10}H_{10}C_2C_6H_5$—$CONH_2$	334	m.p. 111–12°C, i.r. (334)
$B_{10}H_{10}C_2(CONH_2)_2$	9	m.p. 111–13°C
$B_{10}H_{10}C_2(CH_2CONH_2)_2$	9	m.p. 212–15°C

(i) *C*-substituted Amine and Other Nitrogen Derivatives

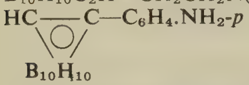
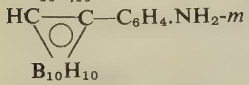
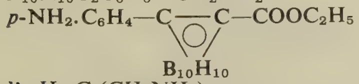
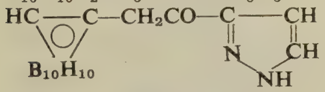
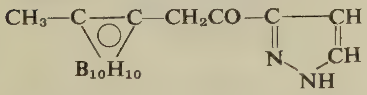
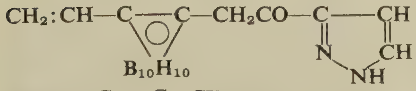
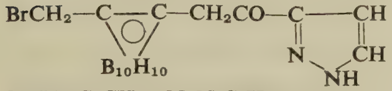
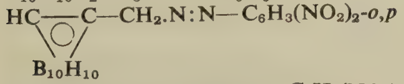
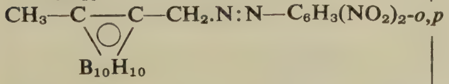
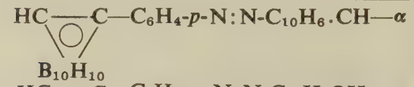
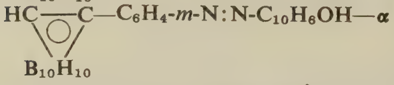
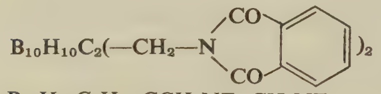
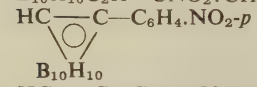
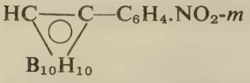
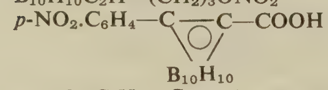
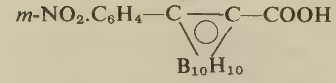
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H$—NH_2	9, 346	m.p. 304–5°C
$B_{10}H_{10}C_2H$—NHC_6H_5	327	m.p. 98–9°C
$B_{10}H_{10}C_2H$—$CH_2N(C_2H_5)_2$	9, 30	m.p. 36°C
$B_{10}H_{10}C_2H$—$CH_2N(C_2H_5)_2,HCl$	9, 30	m.p. >300°C
$B_{10}H_{10}C_2H$—$CH_2CH_2N(C_2H_5)_2$	286, 343	m.p. 46–8°C
 $\underset{B_{10}H_{10}}{HC\text{——}C}\text{—}C_6H_4.NH_2\text{-}p$	174, 310, 324	m.p. 104–5°C, pK_a 3·31 (310)
 $\underset{B_{10}H_{10}}{HC\text{——}C}\text{—}C_6H_4.NH_2\text{-}m$	174, 310, 324	m.p. 83–4°C, pK_a 3·44 (310)
$B_{10}H_{10}C_2CH_3$—NH_2	9, 346	m.p. 302–3°C
$B_{10}H_{10}C_2C_6H_5$—NH_2	174, 346	m.p. 98–9°C
$B_{10}H_{10}C_2C_6H_5$—CH_2NH_2	332	m.p. 61–2°C
 $p\text{-}NH_2.C_6H_4\text{—}\underset{B_{10}H_{10}}{C\text{——}C}\text{—}COOC_2H_5$	312	m.p. 101–2°C
$B_{10}H_{10}C_2(CH_2NH_2)_2$	201	m.p. 247–8°C, pK_a 7·22 (201)
$(B_{10}H_{10}C_2C_6H_5)_2NH$	174	m.p. 239–41°C
$B_{10}H_{10}C_2H$—$CH:NC_6H_5$	327	m.p. 46–7°C
$B_{10}H_{10}C_2CH_3$—$CH:NC_6H_5$	327	m.p. 67–8°C
$B_{10}H_{10}C_2(NHCOOCH_3)_2$	9, 240	m.p. 257–8°C
$B_{10}H_{10}C_2(COON_2H_5)_2$	9	m.p. 90°C decomp.
$B_{10}H_{10}C_2C_6H_5$—NH_2OH	174	m.p. 98–9°C
$B_{10}H_{10}C_2CH_3$—$CSNHC_6H_5$	379	m.p. 80–1°C
 $\underset{B_{10}H_{10}}{HC\text{——}C}\text{—}CH_2CO\text{—}C\text{——}CH$	338	m.p. 130–1°C
 $CH_3\text{—}\underset{B_{10}H_{10}}{C\text{——}C}\text{—}CH_2CO\text{—}C\text{——}CH$	338	m.p. 164–5°C
 $CH_2:CH\text{—}\underset{B_{10}H_{10}}{C\text{——}C}\text{—}CH_2CO\text{—}C\text{——}CH$	338	m.p. 197–8°C
 $BrCH_2\text{—}\underset{B_{10}H_{10}}{C\text{——}C}\text{—}CH_2CO\text{—}C\text{——}CH$	338	m.p. 144–5°C
$B_{10}H_{10}C_2CH_3$—$N:N.C_6H_5$	9	m.p. 115°C
 $\underset{B_{10}H_{10}}{HC\text{——}C}\text{—}CH_2.N:N\text{—}C_6H_3(NO_2)_2\text{-}o,p$	9	m.p. 177–9°C
 $CH_3\text{—}\underset{B_{10}H_{10}}{C\text{——}C}\text{—}CH_2.N:N\text{—}C_6H_3(NO_2)_2\text{-}o,p$	9	m.p. 185°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $HC—C(B_{10}H_{10})—C_6H_4\text{-}p\text{-}N{:}N\text{-}C_{10}H_6.CH—\alpha$	174, 324	m.p. 231–2°C, u.v. (174)
 $HC—C(B_{10}H_{10})—C_6H_4\text{-}m\text{-}N{:}N\text{-}C_{10}H_6OH—\alpha$	174, 324	m.p. 203°C, u.v. (174)
	9	m.p. 328–30°C
$B_{10}H_{10}C_2H—CCH_3NF_2.CH_2NF_2$	344	b.p. 95°C, ^{1}H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H—CCH_3NF_2.CN$	344	m.p. 58°C, ^{1}H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2C_6H_5—CN$	332	m.p. 105–6°C
$B_{10}H_{10}C_2H—CHOH.CN$	327	m.p. 99–100°C
$B_{10}H_{10}C_2H—NCO$	9	
$B_{10}H_{10}C_2(NCO)_2$	9, 240	
$B_{10}H_{10}C_2H—CON_3$	9, 346	m.p. 84–5°C
$B_{10}H_{10}C_2CH_3—CON_3$	9, 346	m.p. 42–3°C
$B_{10}H_{10}C_2C_6H_5—CON_3$	346	m.p. 92–3°C
$B_{10}H_{10}C_2H—CCH_3{:}NOH$	9	m.p. 44–5°C
$B_{10}H_{10}C_2H—NO$	9, 381	m.p. 97°C, i.r. (381), m.s. (381)
$B_{10}H_{10}C_2CH_3—NO$	9, 381	
$B_{10}H_{10}C_2C_6H_5—NO$	174, 379	m.p. 54–5°C
$B_{10}H_{10}C_2H—NO_2$	274	m.p. 100–1°C
$B_{10}H_{10}C_2H—(CH_2)_3NO_2$	9	m.p. 67–9°C
$B_{10}H_{10}C_2H—CCH_3{:}CH—NO_2$	344	m.p. 74°C, i.r. (344), ^{1}H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H—CNO_2{:}CH_2$	9	232°C
 $HC—C(B_{10}H_{10})—C_6H_4.NO_2\text{-}p$	9, 174, 262, 310, 345	m.p. 167–8°C
 $HC—C(B_{10}H_{10})—C_6H_4.NO_2\text{-}m$	174, 310	m.p. 144–5°C
$B_{10}H_{10}C_2H—CCH_3OH.CH_2NO_2$	344	m.p. 103°C, ^{1}H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2H—CCH_3.CH_2NO_2.OOCCH_3$	344	m.p. 84°C, ^{1}H n.m.r. (344), ^{11}B n.m.r. (344)
$B_{10}H_{10}C_2(CH_2ONO_2)_2$	309	m.p. 19–20°C
$B_{10}H_{10}C_2H—(CH_2)_3ONO_2$	9	
 $p\text{-}NO_2.C_6H_4—C—C(B_{10}H_{10})—COOH$	174	
 $m\text{-}NO_2.C_6H_4—C—C(B_{10}H_{10})—COOH$	174	

(j) Miscellaneous *C*-substituted Carbon Derivatives

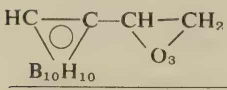
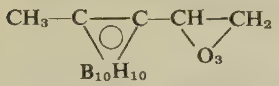
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2C_6H_5^-$	181	$CH_3C_5H_5N^+$ salt: m.p. 149°C
 $HC—C(B_{10}H_{10})—CH—CH_2(O_3)$	330	

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $\underset{B_{10}H_{10}}{CH_3-C-C}-\underset{O_3}{CH-CH_2}$	330	
$B_{10}H_{10}C_2CH_3—CH_2CH(C_8H_{11}O_2)_2$	327	m.p. 207–8°C

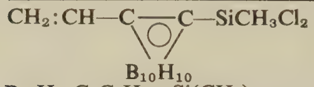
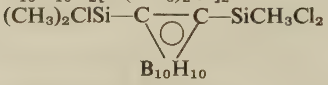
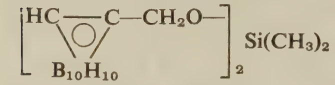
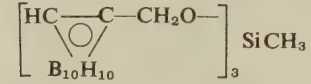
(k) *C*-substituted Boron Compounds

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H—BN(CH_3)_2$	392	m.p. 44–8°C
4-$(B_{10}H_{10}C_2H)$-2:3-$C_2B_9H_{10}$	118	m.p. 156–8°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2H)$-2:3-$C_2(CH_3)_2B_9H_8$	118	m.p. 82–3°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2H)$-1:7-$C_2B_9H_{11}^-$	118	Cs^+ salt: m.p. >360°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2H)$-1:7-$C_2(CH_3)_2B_9H_9^-$	118	Cs^+ salt: m.p. 244–6°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2CH_3)$-2:3-$C_2B_9H_{10}$	118	m.p. 116–18°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2CH_3)$-2:3-$C_2(CH_3)_2B_9H_8$	118	m.p. 101–2°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)
4-$(B_{10}H_{10}C_2CH_3)$-1:7-$C_2B_9H_{11}^-$	118, 131	$(CH_3)_4N^+$ salt: m.p. >360°C, i.r. (118, 131), ^1H n.m.r. (118, 131), ^{11}B n.m.r. (118, 131)
4-$(B_{10}H_{10}C_2CH_3)$-1:7-$C_2(CH_3)_2B_9H_9^-$	118	Cs^+ salt: m.p. 229–31°C, i.r. (118), ^1H n.m.r. (118), ^{11}B n.m.r. (118)

(l) *C*-substituted Silicon Compounds

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H—Si(CH_3)_3$	9, 240, 379	m.p. 94–5°C
$B_{10}H_{10}C_2H—Si(C_6H_5)_3$	9, 240	m.p. 165–7°C
$B_{10}H_{10}C_2H—Si(CH_3)_2OSi(CH_3)_2OH$	259	
$B_{10}H_{10}C_2H—CH_2Si(CH_3)_3$	9, 240	m.p. 52°C
$B_{10}H_{10}C_2H—CH_2SiCH_3Cl_2$	353	
$B_{10}H_{10}C_2H—CH_2SiCH_3(OC_2H_5)_2$	353	
$B_{10}H_{10}C_2H—CH_2CH_2Si(CH_3)_2Cl$	395	m.p. 68°C, b.p. 145–7°C at 3 torr
$B_{10}H_{10}C_2H—CH_2CH_2SiCH_3Cl_2$	395	m.p. 72–3°C, b.p. 149–50°C at 3 torr
$B_{10}H_{10}C_2H—CH_2CH_2SiCl_3$	395	m.p. 90°C, b.p. 138–41°C at 3 torr
$B_{10}H_{10}C_2H—(CH_2)_3SiCH_3(OC_2H_5)_2$	353	b.p. 134–8°C at 0·2 torr
$B_{10}H_{10}C_2H—(CH_2)_4SiCH_3Cl_2$	395	b.p. 187–8°C at 4 torr
$B_{10}H_{10}C_2H—(CH_2)_4SiCH_3(OC_2H_5)_2$	9, 353	b.p. 160–2°C at 0·1 torr
$B_{10}H_{10}C_2H—CH_2CHCH_3SiCH_3Cl_2$	395	m.p. 52–3°C, b.p. 155–6°C at 3 torr
$B_{10}H_{10}C_2H—CH_2CHCH_3SiC_2H_5Cl_2$	395	m.p. 44°C, b.p. 147–8°C at 3 torr
$B_{10}H_{10}C_2H—CH_2CHCH_3SiC_6H_5Cl_2$	395	b.p. 211°C at 3 torr, d_4^{20} 1·1398
$B_{10}H_{10}C_2H—CH_2CHCH_3SiCl_3$	395	m.p. 60°C, b.p. 151–2°C at 3 torr
$B_{10}H_{10}C_2CH_3—SiCH_3Cl_2$	394	m.p. 35–8°C
$B_{10}H_{10}C_2CH_3—SiCH_3(OC_2H_5)_2$	9, 353	b.p. 150–60°C at 0·5 torr
$B_{10}H_{10}C_2CH_3—SiC_6H_5Cl_2$	394	m.p. 53–5°C, b.p. 156°C at 0·06 torr
$B_{10}H_{10}C_2CH_3—CH_2SiCH_3(OC_2H_5)_2$	353	m.p. 260–1°C
$B_{10}H_{10}C_2CH_3—(CH_2)_3SiCH_3Cl_2$	395	b.p. 180–3°C at 5 torr

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 $CH_2{:}CH{-}\underset{B_{10}H_{10}}{C{-}C}{-}SiCH_3Cl_2$	394	m.p. 40–2°C
$B_{10}H_{10}C_2C_6H_5{-}Si(CH_3)_3$	379, 382–3	m.p. 105–6°C
$B_{10}H_{10}C_2[SiH(CH_3)_2]_2$	396	b.p. 121–5°C at 3 torr, n_D^{20} 1·5360 d_4^{20} 0·9457
$B_{10}H_{10}C_2[Si(CH_3)_3]_2$	397	m.p. 141–2°C
$B_{10}H_{10}C_2[Si(CH_3)_2C_6H_5]_2$	397	m.p. 138–9°C
$B_{10}H_{10}C_2[SiCH_3(C_6H_5)_2]_2$	397	m.p. 241–3°C
$B_{10}H_{10}C_2[Si(CH_3)_2Cl]_2$	258	m.p. 113°C
 $(CH_3)_2ClSi{-}\underset{B_{10}H_{10}}{C{-}C}{-}SiCH_3Cl_2$	258	m.p. 119–20°C, isomerization kinetics (397)
$B_{10}H_{10}C_2[Si(C_6H_5)_2Cl]_2$	258	m.p. 244–5°C
$B_{10}H_{10}C_2(SiCl_3)_2$	258	m.p. 121–2°C
$B_{10}H_{10}C_2[CH_2OSi(CH_3)_3]_2$	9, 353	m.p. 146°C, b.p. 135°C at 0·5 torr
$B_{10}H_{10}C_2[OSi(CH_3)_2OSi(CH_3)_2OC_4H_9]_2$	396	b.p. 110–15°C at 10 torr
$(B_{10}H_{10}C_2H{-})_2Si(CH_3)_2$	9, 240	m.p. 195–7°C
 $\left[\underset{B_{10}H_{10}}{HC{-}C}{-}CH_2O{-}\right]_2Si(CH_3)_2$	9, 353	m.p. 98–100°C
 $\left[\underset{B_{10}H_{10}}{HC{-}C}{-}CH_2O{-}\right]_3SiCH_3$	353	m.p. 220°C
$(B_{10}H_{10}C_2C_6H_5{-})_2SiCl_2$	383	m.p. 179–80°C, i.r. (283)

(m) *C*-substituted Germanium and Tin Derivatives

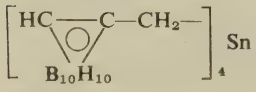
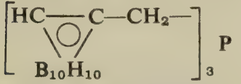
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2[Ge(CH_3)_2Cl]_2$	398	m.p. 118°C
$(B_{10}H_{10}C_2C_6H_5{-})_2GeCl_2$	383	m.p. 205–6°C, i.r. (283)
$B_{10}H_{10}C_2H{-}Sn(C_3H_7)_3$	383	b.p. 148–50°C at 1 torr, n_D^{20} 1·5470, Mössbauer spectrum (399)
$B_{10}H_{10}C_2H{-}Sn(C_6H_5)_3$	181	m.p. 161–3°C, i.r. (283), Mössbauer spectrum (399)
$B_{10}H_{10}C_2C_6H_5{-}Sn(C_3H_7)_3$	181	m.p. 128–30°C, i.r. (283), Mössbauer spectrum (399)
$B_{10}H_{10}C_2C_6H_5{-}Sn(C_6H_5)_3$	379, 382–3	m.p. 186–7°C, Mössbauer spectrum (399)
$B_{10}H_{10}C_2[Sn(C_3H_7)_3]_2$	383	m.p. 42–3°C, Mössbauer spectrum (399)
$B_{10}H_{10}C_2[Sn(C_6H_5)_3]_2$	399	Mössbauer spectrum (399)
$B_{10}H_{10}C_2[Sn(C_6H_5)_2Cl]_2$	398	m.p. 143–4°C
$(B_{10}H_{10}C_2C_6H_5{-})_2Sn(C_4H_9)_2$	181	m.p. 149–50°C, i.r. (283), Mössbauer spectrum (399)
$(B_{10}H_{10}C_2C_6H_5{-})_2SnO$	181	m.p. 218–20°C, decomp.
$(B_{10}H_{10}C_2C_6H_5{-})_2SnCl_2$	383	m.p. 216–18°C, i.r. (283), Mössbauer spectrum (399)
$(B_{10}H_{10}C_2C_6H_5{-})_2SnBr_2$	181, 383	m.p. 203–4°C, i.r. (283), Mössbauer spectrum (399)
$(B_{10}H_{10}C_2C_6H_5{-})_3SnCl$	383	m.p. 287–8°C, Mössbauer spectrum (399)
 $\left[\underset{B_{10}H_{10}}{HC{-}C}{-}CH_2{-}\right]_4Sn$	385	m.p. >350°C

Table XXVIII.—continued

(n) *C*-substituted Phosphorus, Arsenic and Antimony Compounds

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2C_6H_5—P(C_6H_{13})_2$	382–3	m.p. 9–10°C
$B_{10}H_{10}C_2[P(C_2H_5)_2]_2$	400	m.p. 56–8°C
$B_{10}H_{10}C_2[P(C_6H_5)_2]_2$	260, 379, 402	m.p. 219°C
$B_{10}H_{10}C_2(PC_6H_5Cl)_2$	260	m.p. 172–4°C, i.r. (260)
$B_{10}H_{10}C_2(PC_6H_5N_3)_2$	260	m.p. 126–8°C
$(B_{10}H_{10}C_2C_6H_5—)_2PCl$	383	m.p. 226–7°C, i.r. (283)
 $\left[\underset{B_{10}H_{10}}{HC—C}—CH_2—\right]_3P$	385	
$9\text{-}B_{10}H_9ClC_2[P(C_6H_5)_2]_2$	402	m.p. 201–3°C
$9{:}12\text{-}B_{10}H_8Cl_2C_2[P(C_6H_5)_2]_2$	402	m.p. 228–30°C
$8{:}9{:}12\text{-}B_{10}H_7Cl_3C_2[P(C_6H_5)_2]_2$	402	m.p. 215–17°C
$B_{10}H_9BrC_2[P(C_6H_5)_2]_2$	363	m.p. 217–19°C
$B_{10}H_8Br_2C_2[P(C_6H_5)_2]_2$	363	m.p. 235–7°C
$B_{10}H_7Br_3C_2[P(C_6H_5)_2]_2$	363	m.p. 236–8°C
$B_{10}H_8Br_2C_2(PC_6H_5Cl)_2$	363	m.p. 199–200°C
$B_{10}H_8Br_2C_2(PC_6H_5N_3)_2$	363	m.p. 125°C decomp.
$B_{10}H_{10}C_2[As(CH_3)_2]_2$	288, 408	m.p. 111°C, i.r. (288, 408), ^1H n.m.r. (408), ^{11}B n.m.r. (408)
$B_{10}H_{10}C_2[As(C_6H_5)_2]_2$	288	m.p. 205°C, i.r. (288)
$(B_{10}H_{10}C_2C_6H_5—)_3As$	383	m.p. 175–6°C, i.r. (283)
$(B_{10}H_{10}C_2C_6H_5—)_3Sb$	383	m.p. 313–16°C, i.r. (283)

(o) *C*-substituted Sulphur Compounds

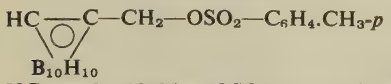
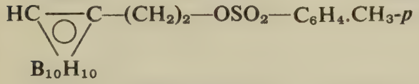
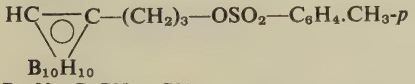
Formula	Preparation references	Properties and references
 $\underset{B_{10}H_{10}}{HC—C}—CH_2—OSO_2—C_6H_4.CH_3\text{-}p$	9	m.p. 106–8°C
 $\underset{B_{10}H_{10}}{HC—C}—(CH_2)_2—OSO_2—C_6H_4.CH_3\text{-}p$	9	m.p. 64–6°C
 $\underset{B_{10}H_{10}}{HC—C}—(CH_2)_3—OSO_2—C_6H_4.CH_3\text{-}p$	9	m.p. 119–21°C
$B_{10}H_{10}C_2CH_3—SH$	379	m.p. 245–6°C
$B_{10}H_{10}C_2CH_3—CSNHC_6H_5$	341, 379	m.p. 80–1°C
$B_{10}H_{10}C_2CH_3—CH_2CHOH.SO_3Na$	327	m.p. 168–70°C
$B_{10}H_{10}C_2C_6H_5—CSNHC_6H_5$	341	m.p. 121–2°C
$B_{10}H_{10}C_2(SH)_2$	379, 409	m.p. 265–7°C
$B_{10}H_{10}C_2(SCH_3)_2$	409	m.p. 101–2°C
$B_{10}H_{10}C_2(SC_6H_5)_2$	409	m.p. 189–91°C
$B_{10}H_{10}C_2(SCH_2C_6H_5)_2$	409	m.p. 102–4°C
$B_{10}H_{10}C_2(SCl)_2$	412	m.p. 79–80°C
$B_{10}H_{10}C_2(CH_2OSO_2CH_3)_2$	411	
$B_{10}H_{10}C_2(SCONHC_6H_5)_2$	410	m.p. 131–3°C
$B_{10}H_9BrC_2(SH)_2$	409	m.p. 138–40°C
$B_{10}H_7Br_3C_2(SH)_2$	409	m.p. 203–6°C
$B_{10}H_8Br_2C_2(SCH_3)_2$	409	m.p. 181–3°C
$B_{10}H_8Br_2C_2(SC_2H_5)_2$	409	m.p. 95–7°C

Table XXVIII.—continued

(p) *C*-substituted Metal Reagents—Preparation Details

Formula	Preparation references
$B_{10}H_{10}C_2RLi$	347
$B_{10}H_{10}C_2Li_2$	186, 260, 347
$B_{10}H_{10}C_2HNa$	316, 351
$B_{10}H_{10}C_2Na_2$	351
$B_{10}H_{10}C_2H—CH_2MgBr$	199, 240
$B_{10}H_{10}C_2CH_3—MgBr$	186
$B_{10}H_{10}C_2(CH_2MgCl)_2$	240

(q) *C*-substituted Mercury Derivatives

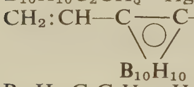
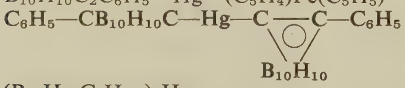
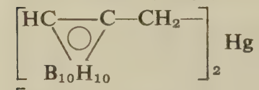
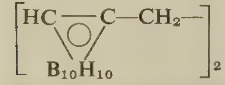
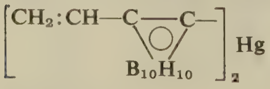
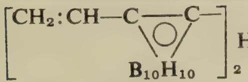
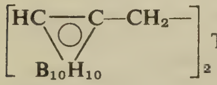
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H—HgCH_3$	379, 383, 389	m.p. 205–6°C
$B_{10}H_{10}C_2H—CH_2HgCl$	385	m.p. 217–18°C
$B_{10}H_{10}C_2H—CH_2HgCl$.(*o*-phenanthroline)	390	m.p. >240°C decomp.
$B_{10}H_{10}C_2CH_3—HgCH_3$	379, 384, 389	m.p. 76–7 or 167–8°C
$B_{10}H_{10}C_2CH_3—HgC_6H_5$	379	m.p. 137–8°C
$B_{10}H_{10}C_2CH_3—HgCl$	379, 390	m.p. 217–19 or 272–3°C
$B_{10}H_{10}C_2CH_3—HgCl$.(*o*-phenanthroline)	390	m.p. 271–2°C
$B_{10}H_{10}C_2CH_3—HgBr$.(2,2′-bipyridyl)	388	m.p. 218–20°C decomp.
$B_{10}H_{10}C_2CH_3—HgOH$	388	m.p. 131–7°C
 $CH_2{:}CH—\underset{B_{10}H_{10}}{C—C}—Hg—CH_3$	383	m.p. 100–1°C
$B_{10}H_{10}C_2C_6H_5—HgCH_3$	382–3, 389	m.p. 159–60°C, *X*-ray (254)
$B_{10}H_{10}C_2C_6H_5—HgC_6H_5$	384, 387, 389	m.p. 187–8°C
$B_{10}H_{10}C_2C_6H_5—HgCH_3$.(*o*-phenanthroline)	390	m.p. 190–1°C
$B_{10}H_{10}C_2C_6H_5—HgCl$	379, 384, 387	m.p. 188–9°C
$B_{10}H_{10}C_2C_6H_5—HgCl$.(*o*-phenanthroline)	390	m.p. >240°C decomp.
$B_{10}H_{10}C_2C_6H_5—HgBr$	383	m.p. 173–4°C, *X*-ray (254)
$B_{10}H_{10}C_2C_6H_5—HgBr$.(2,2′-bipyridyl)	388	m.p. 183–4°C decomp.
$B_{10}H_{10}C_2C_6H_5—HgOH$	388	m.p. 136–42°C
$B_{10}H_{10}C_2C_6H_5—Hg—(C_5H_4)Fe(C_5H_5)$	384, 387	m.p. 137–8°C
 $C_6H_5—CB_{10}H_{10}C—Hg—\underset{B_{10}H_{10}}{C—C}—C_6H_5$	386	m.p. 159–60°C
$(B_{10}H_{10}C_2H—)_2Hg$	383, 391	m.p. >400°C, i.r. (282), polarography (391)
$(B_{10}H_{10}C_2H—)_2Hg$.(2,2′-bipyridyl)	388	
 $\left[\underset{B_{10}H_{10}}{HC—C}—CH_2—\right]_2Hg$	9, 385	m.p. 280–2°C decomp.
 $\left[\underset{B_{10}H_{10}}{HC—C}—CH_2—\right]_2$ **Hg.(*o*-phenanthroline)**	390	m.p. 150–2°C decomp.
$(B_{10}H_{10}C_2CH_3—)_2Hg$	9, 379, 383	m.p. >300°C, polarography (391)
$(B_{10}H_{10}C_2CH_3—)_2Hg$.(2,2′-bipyridyl)	388	m.p. 252–4°C decomp.
$(B_{10}H_{10}C_2CH_3—)_2Hg$.(*o*-phenanthroline)	390	m.p. >285°C decomp.
 $\left[CH_2{:}CH—\underset{B_{10}H_{10}}{C—C}—\right]_2Hg$	383–4	m.p. 153–4°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
 Hg.(2:2′-bipyridyl)	388	m.p. 254–5°C decomp.
$(B_{10}H_{10}C_2C_6H_5)_2Hg$	383, 386, 387, 391	m.p. 262–3°C, *X*-ray (254), polarography (391)
$(B_{10}H_{10}C_2C_6H_5—)_2Hg.$(2,2′-bipyridyl)	388	m.p. 244–5°C decomp.
$(B_{10}H_{10}C_2C_6H_5—)_2Hg.$(*o*-phenanthroline)	390	m.p. >268°C decomp.
$(9{:}12\text{-}B_{10}H_8Cl_2C_2H—)_2Hg$	391	m.p. 308–10°C, polarography (391)
$(9{:}12\text{-}B_{10}H_8Cl_2C_2CH_3—)HgCH_3$	389	m.p. 265°C
$9{:}12\text{-}B_{10}H_8Br_2C_2CH_3—HgCH_3$	389	m.p. 263°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2CH_3—HgCH_3$	389	m.p. 322°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2CH_3—HgC_6H_5$	389	m.p. 254°C

(r) *C*-substituted Derivatives of Other Metals

Formula	Preparation references	Properties and references
 $Ti(C_5H_5)_2$	385	m.p. 185°C decomp.
$B_{10}H_{10}C_2CH_3—Fe(C_5H_5)(CO)_2$	128, 492	m.p. 144–5°C, ^1H n.m.r. (128), u.v. (128)
$B_{10}H_{10}C_2CH_3—Pt[P(C_2H_5)_3]_2$	414	m.p. 146–7°C
$B_{10}H_{10}C_2C_6H_5—Pt[P(C_2H_5)_3]_2$	414	m.p. 196–7°C
$(B_{10}H_{10}C_2C_6H_5)_2Zn$	356	

(s) Exocyclic Carbon Derivatives

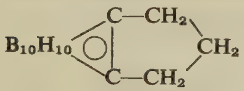
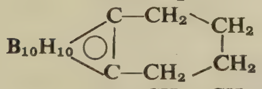
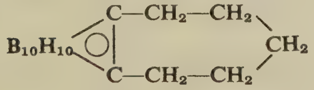
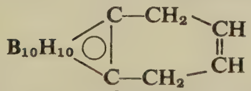
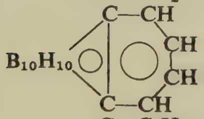
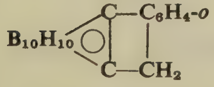
Formula	Preparation references	Properties and references
	366–7	m.p. 197–8°C, i.r. (367)
	366	m.p. 122–3°C
	366	m.p. 98–9°C
	365	m.p. 113–14°C, ^1H n.m.r. (365)
	365	m.p. 110°C, ^1H n.m.r. (365), u.v. (365, 542)
	312–13	m.p. 133–4°C, ^1H n.m.r. (313)

Table XXVIII.—continued

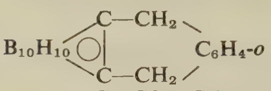
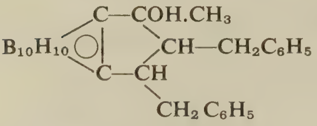
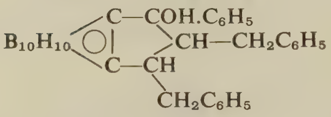
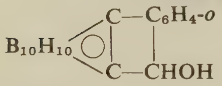
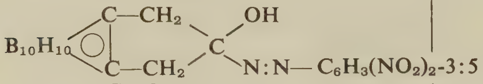
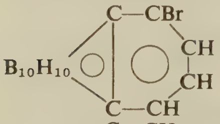
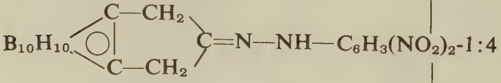
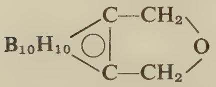
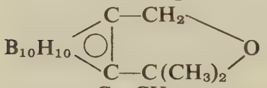
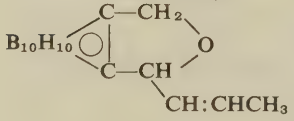
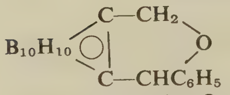
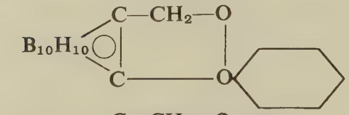
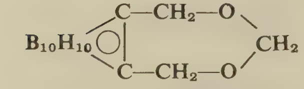
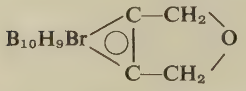
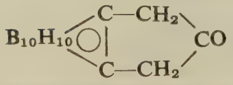
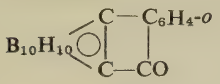
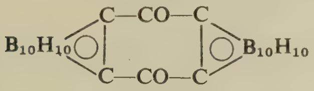
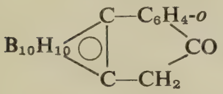
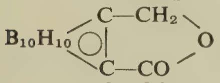
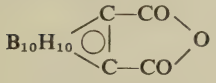
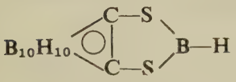
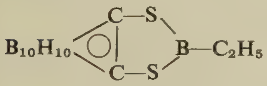
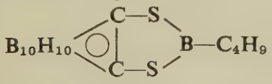
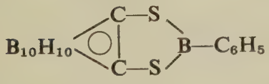
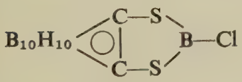
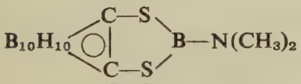
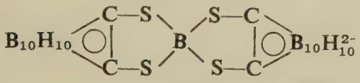
Formula	Preparation references	Properties and references
	362	m.p. 182–4°C
	329	m.p. 140–1°C, ^{1}H n.m.r. (329)
	329	m.p. 165–6°C, ^{1}H n.m.r. (329)
	312–13	m.p. 142–3°C
	260	
	365	m.p. 90–2°C, ^{1}H n.m.r. (365)
	9	m.p. 122°C decomp.
	9, 186, 240	i.r. (450)
	350	m.p. 61–2°C
	14, 350	m.p. 71–2°C
	14, 350	m.p. 92–3°C
	14, 350	m.p. 76–7°C
	326	m.p. 88–9°C, i.r. (326)
	9, 186, 240	m.p. 127–9°C
	9, 240	sublimes 170°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	286, 312–13	m.p. 165–6°C, i.r. (450)
	376	m.p. 315°C, i.r. (376)
	366	m.p. 142–4°C
	186, 257	m.p. 253–5°C
	9, 240	m.p. 180°C

(t) Exocyclic Boron Derivatives

Formula	Preparation references	Properties and references
	410	m.p. 42–50°C
	410	m.p. 44–7°C, b.p. 78°C at 0·25 torr
	410	b.p. 91°C at 0·15 torr, ^{1}H n.m.r. (410), ^{11}B n.m.r. (410)
		
	410	m.p. 62–4°C
	410	m.p. 137–9°C
	410	$(C_2H_5)_4N^+$ salt: m.p. 320°C

(u) Exocyclic Silicon, Germanium and Tin Derivatives

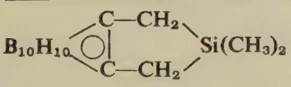
Formula	Preparation references	Properties and references
	9, 240	m.p. 149–50°C

Table XXVIII.—continued

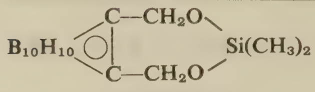
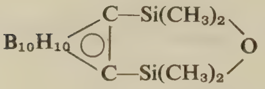
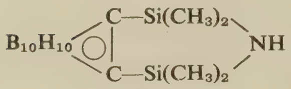
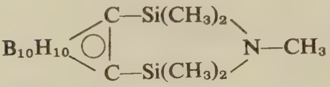
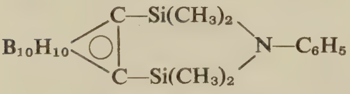
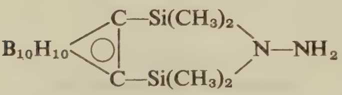
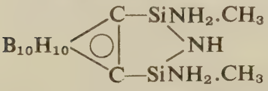
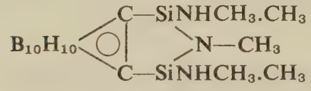
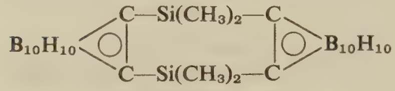
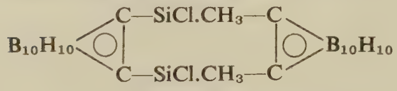
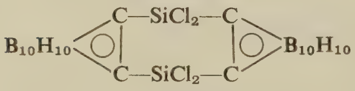
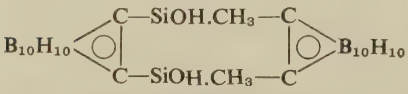
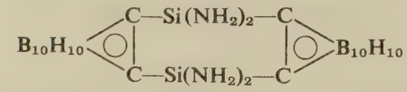
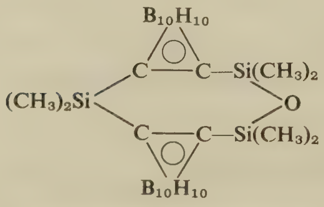
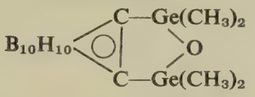
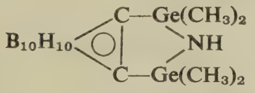
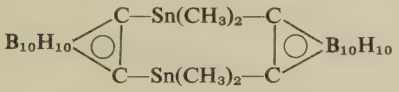
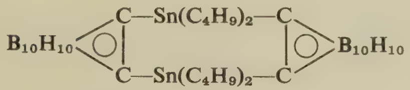
Formula	Preparation references	Properties and references
	9, 353, 483	m.p. 98–100°C, b.p. 100°C at 0·02 torr
	258	m.p. 160–1°C, i.r. (259)
	258	m.p. 190–2°C
	259	m.p. 156–8°C
	259	m.p. 183–5°C
	259	m.p. 163–5°C
	258	m.p. 189–92°C
	258	m.p. 128–30°C
	258	m.p. 309–10°C
	259	m.p. 281–3°C
	258	m.p. 271–2°C
	259	m.p. 304°C
	259	m.p. 347–9°C
	259	m.p. 207–8°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	398	m.p. 202–4°C
	398	m.p. 166–8°C
	398	m.p. 352–5°C
	383	m.p. 186–7°C, Mössbauer spectrum (399)

(v) Exocyclic Phosphorus and Arsenic Derivatives and their Metal Complexes

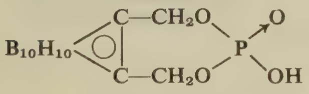
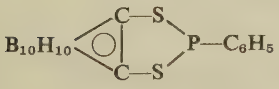
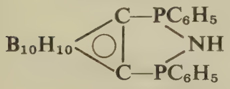
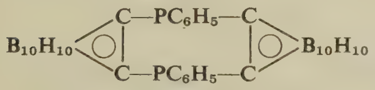
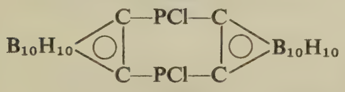
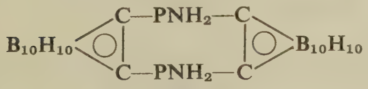
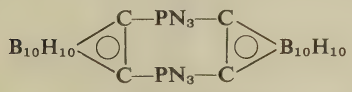
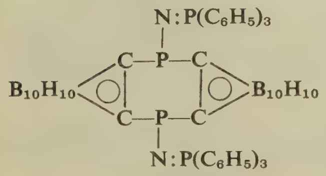
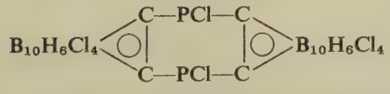
Formula	Preparation references	Properties and references
	403	m.p. 259–60°C, i.r. (403)
	409	m.p. 158–60°C
	260, 404	m.p. 222–4°C
	260	m.p. 356–8°C
	260, 404	m.p. 240–1°C, i.r. (260)
	260	m.p. 280°C
	260, 404	m.p. 150°C decomp.
	260	m.p. 311–12°C
	363	m.p. 426–7°C

Table XXVIII.—continued

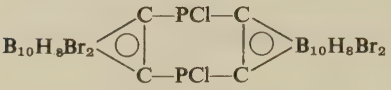
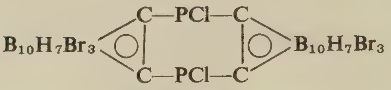
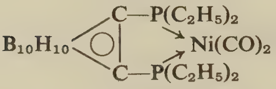
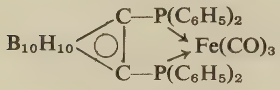
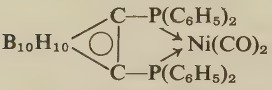
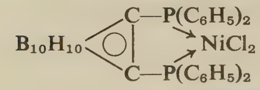
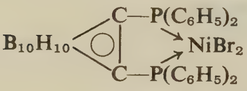
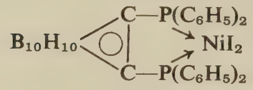
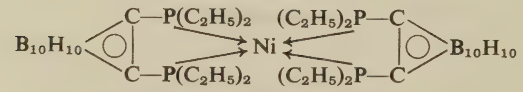
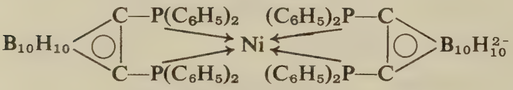
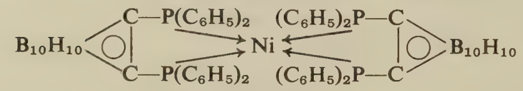
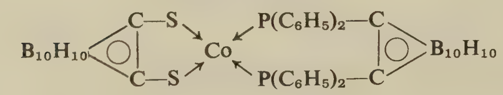
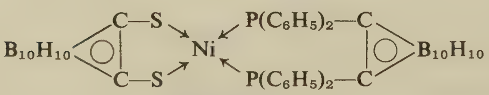
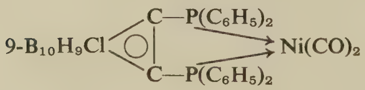
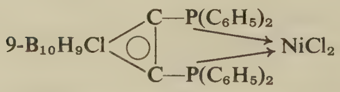
Formula	Preparation references	Properties and references
	363	m.p. 415°C
	363	m.p. 412–14°C
	400	m.p. 119–20°C
	406	m.p. 243–5°C
	400, 402, 406	m.p. 205–8°C decomp.
	402, 405–7	m.p. 340°C decomp., u.v. (407), molar conductance (407)
	402	
	402, 406	m.p. 338–40°C
	400	m.p. 287–90°C decomp.
	405	molar conductance (405)
	400, 402	m.p. 267–80°C
	407	m.p. 353°C, u.v. (407), μ_{eff} $19{\cdot}2 \times 10^{-24}$ Am^2 (2·08 B.M.) (407), molar conductance (407)
	407	m.p. 380°C decomp., u.v. (407), molar conductance (407)
	402	m.p. 206°C decomp.
	402	m.p. 250°C decomp.

Table XXVIII.—continued

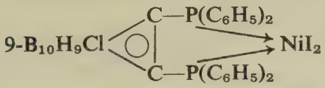
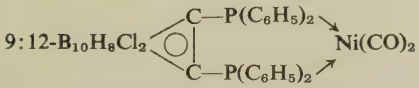
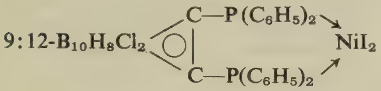
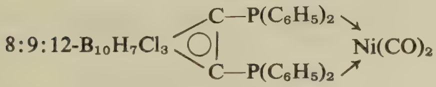
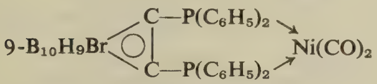
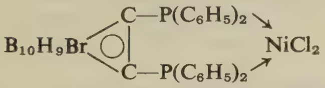
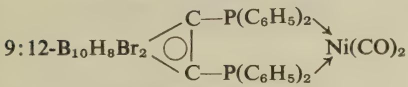
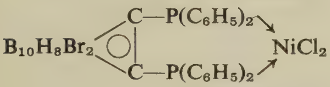
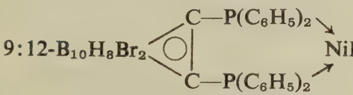
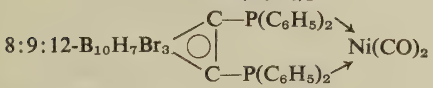
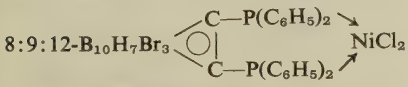
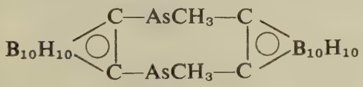
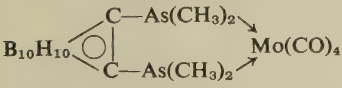
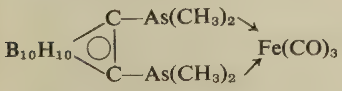
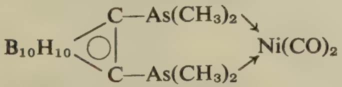
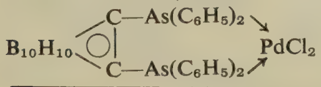
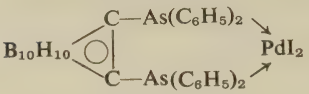
Formula	Preparation references	Properties and references
	402	
	402	m.p. 222–4°C
	402	
	402	m.p. 200°C decomp.
	402	m.p. 198–9°C
	405	u.v. (501), molar conductance (501)
	402	m.p. 235°C decomp.
	405	u.v. (501), molar conductance (501)
	402	
	402	m.p. 240°C decomp.
	402, 405	m.p. 245°C decomp., u.v. (501), molar conductance (501)
	408	m.p. 215–21°C, i.r. (408), ^{1}H n.m.r. (408)
	408	i.r. (408), ^{1}H n.m.r. (408)
	408	i.r. (408), ^{1}H n.m.r. (408), Mössbauer spectrum (408)
	408	i.r. (408), ^{1}H n.m.r. (408)
	288	m.p. 225°C, i.r. (288)

Table XXVIII.—*continued*

Formula	Preparation references	Properties and references
	288	m.p. 329°C decomp., i.r. (288)

(w) Exocyclic Sulphur Derivatives and their Metal Complexes

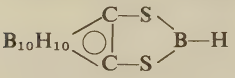
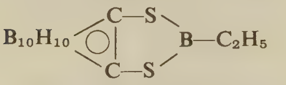
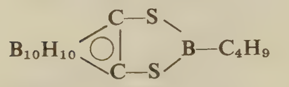
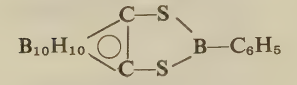
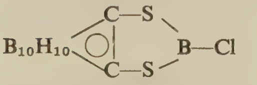
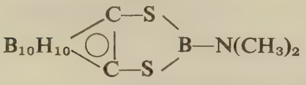
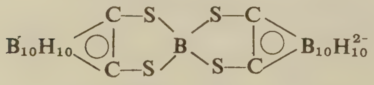
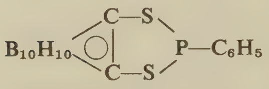
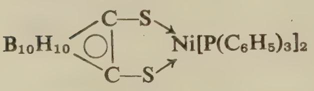
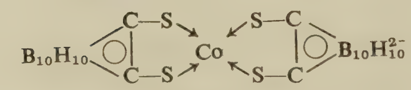
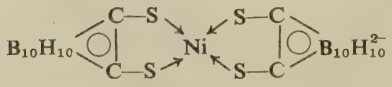
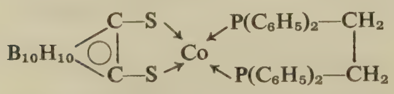
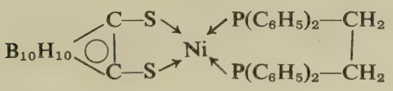
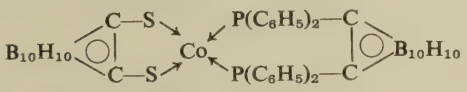
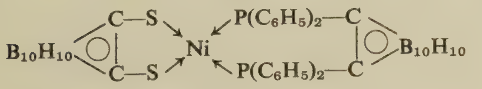
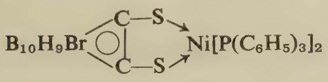
Formula	Preparation references	Properties and references
	410	m.p. 42–50°C
	410	m.p. 44–7°C, b.p. 78°C at 0·25 torr
	410	b.p. 91°C at 0·15 torr, ^{1}H n.m.r. (410), ^{11}B n.m.r. (410)
	410	m.p. 90–100°C
	410	m.p. 62–4°C
	410	m.p. 137–9°C
	410	$(C_2H_5)_4N^+$ salt: m.p. 320°C
	409	m.p. 158–60°C
	407, 409	m.p. 250°C decomp., u.v. (407), molar conductance (407)
	407, 413	$(C_2H_5)_4N^+$ salt: m.p. 340°C, u.v. (407), molar conductance (407), μ_{eff} 27·8 × 10^{-24} Am^2 (5·20 B.M.)
	407, 413	$(C_2H_5)_4N^+$ salt: m.p. 320°C, u.v. (407), molar conductance (407)
	407	m.p. 350°C, u.v. (407), molar conductance (407)

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	407	m.p. 375°C decomp., u.v. (407) molar conductance (407)
	407	m.p. 353°C, u.v. (407), molar conductance (407), μ_{eff} $19{\cdot}2 \times 10^{-24}$ Am^2 (2·08 B.M.)
	407	m.p. 380°C decomp., u.v. (407), molar conductance (407)
	407	m.p. 234°C decomp.

(x) Polyfunctional *C*-substituted Derivatives

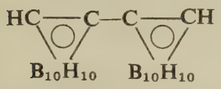
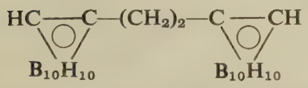
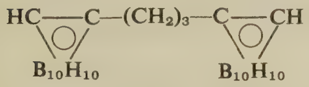
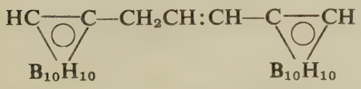
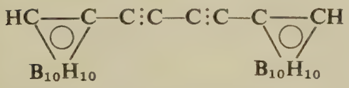
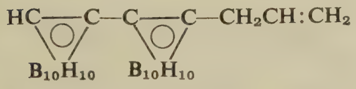
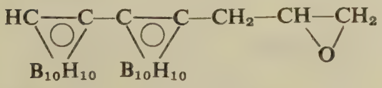
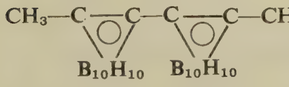
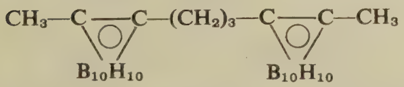
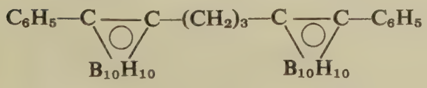
Formula	Preparation references	Properties and references
	9, 200, 248	m.p. 309–10 or 380°C, i.r. (282), *X*-ray (248)
	9	m.p. > 250°C
	9, 31	m.p. 355–7°C
	240	m.p. > 300°C
	9	m.p. 303–4°C
	9	m.p. 125–6°C
	9	m.p. 173–4°C
	9, 200	m.p. 193–4°C
	362	m.p. 352–3°C
	362	m.p. 205–6°C

Table XXVIII.—continued

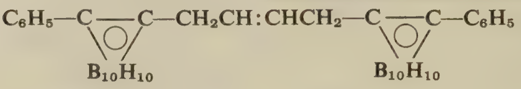
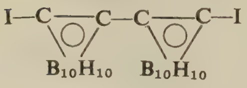
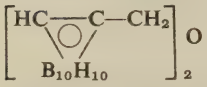
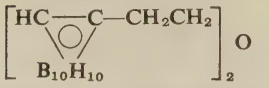
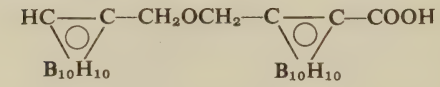
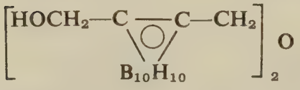
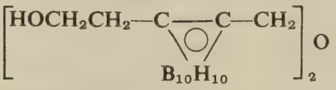
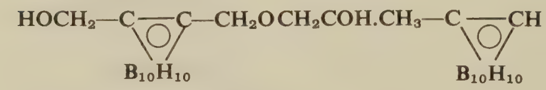
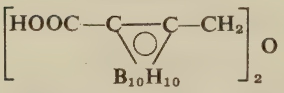
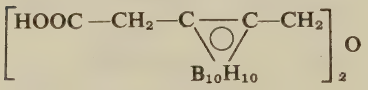
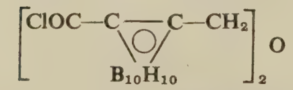
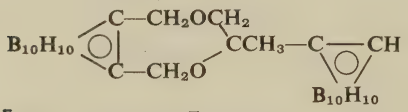
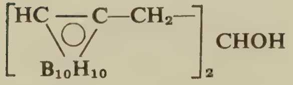
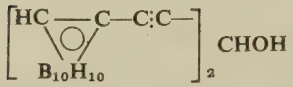
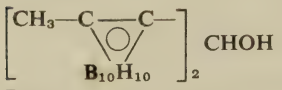
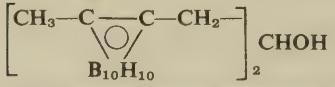
Formula	Preparation references	Properties and references
	362	m.p. 182–3°C
	9, 200	m.p. 183–4°C
	9, 257, 286	m.p. 355–63°C
	257	m.p. 117–18°C
	257	m.p. 73°C
	257	m.p. >350°C
	257	m.p. 126–8°C
	318	m.p. 196–201°C, ^{1}H n.m.r. (318), ^{11}B n.m.r. (318)
	9, 257	m.p. 235–6°C
	257	m.p. 242–4°C
	257	m.p. 186–9°C
	318	m.p. 249–51°C
	9, 335	m.p. 116–17°C
	9	m.p. 175–6°C
	329, 341	m.p. 177–8°C
	335	m.p. 331–2°C

Table XXVIII.—continued

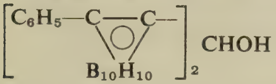
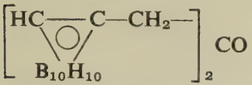
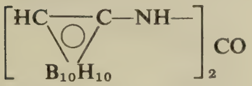
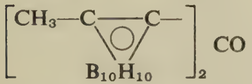
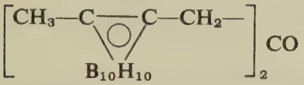
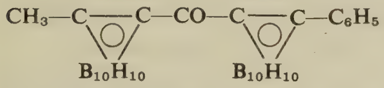
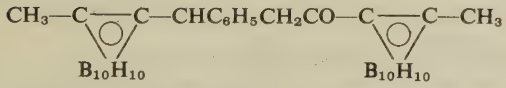
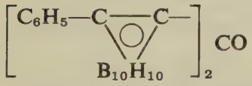
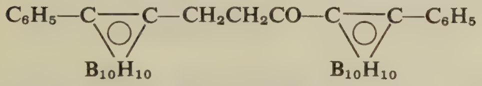
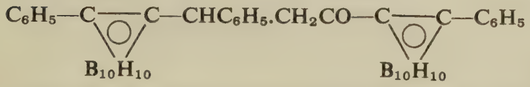
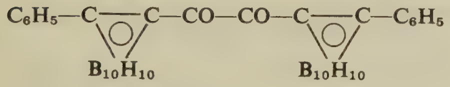
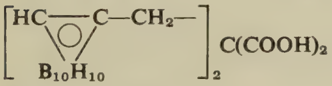
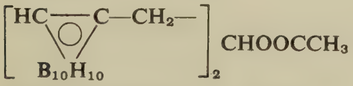
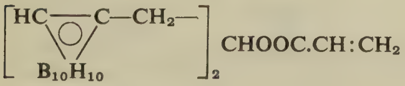
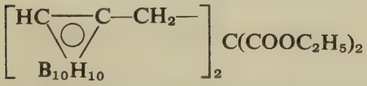
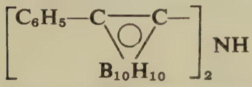
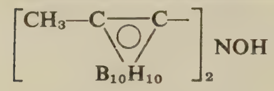
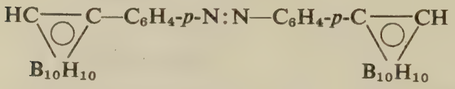
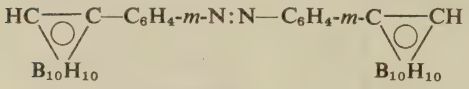
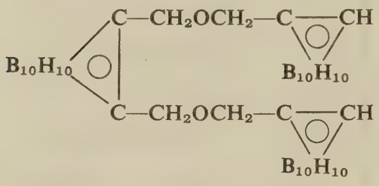
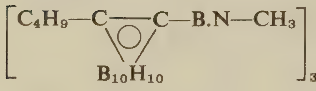
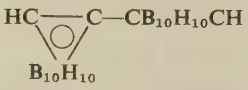
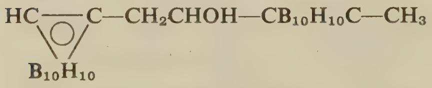
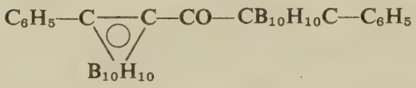
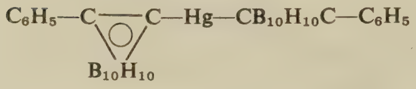
Formula	Preparation references	Properties and references
 $\left[C_6H_5-\underset{B_{10}H_{10}}{C-C}-\right]_2CHOH$	321, 329, 341, 354	m.p. 282–3°C
 $\left[\underset{B_{10}H_{10}}{HC-C}-CH_2-\right]_2CO$	9	m.p. >250°C
 $\left[\underset{B_{10}H_{10}}{HC-C}-NH-\right]_2CO$	9	m.p. 245°C
 $\left[CH_3-\underset{B_{10}H_{10}}{C-C}-\right]_2CO$	372	m.p. 144–5°C
 $\left[CH_3-\underset{B_{10}H_{10}}{C-C}-CH_2-\right]_2CO$	335	m.p. 306–7°C
 $CH_3-\underset{B_{10}H_{10}}{C-C}-CO-\underset{B_{10}H_{10}}{C-C}-C_6H_5$	372	m.p. 150°C
 $CH_3-\underset{B_{10}H_{10}}{C-C}-CHC_6H_5CH_2CO-\underset{B_{10}H_{10}}{C-C}-CH_3$	340–1	m.p. 155–6°C
 $\left[C_6H_5-\underset{B_{10}H_{10}}{C-C}-\right]_2CO$	372	m.p. 217°C
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CH_2CH_2CO-\underset{B_{10}H_{10}}{C-C}-C_6H_5$	328	m.p. 177–8°C
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CHC_6H_5.CH_2CO-\underset{B_{10}H_{10}}{C-C}-C_6H_5$	340–1	m.p. 201–2°C
 $C_6H_5-\underset{B_{10}H_{10}}{C-C}-CO-CO-\underset{B_{10}H_{10}}{C-C}-C_6H_5$	321, 372	m.p. 178–80°C
 $\left[\underset{B_{10}H_{10}}{HC-C}-CH_2-\right]_2C(COOH)_2$	186	
 $\left[\underset{B_{10}H_{10}}{HC-C}-CH_2-\right]_2CHOOCCH_3$	240	m.p. 206–8°C
 $\left[\underset{B_{10}H_{10}}{HC-C}-CH_2-\right]_2CHOOC.CH{:}CH_2$		m.p. 148–50°C
 $\left[\underset{B_{10}H_{10}}{HC-C}-CH_2-\right]_2C(COOC_2H_5)_2$	9, 199	m.p. 199–202°C
 $\left[C_6H_5-\underset{B_{10}H_{10}}{C-C}-\right]_2NH$	174	m.p. 368–72°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	9	m.p. 203–5°C
	324	m.p. 231–2°C
	324	m.p. 203–4°C
	9	m.p. 368–72°C
	392	waxy material

(y) *C*-substituted *closo*-1:7-dicarbadodecaborane(12) Derivatives of 1:2-$C_2B_{10}H_{12}$

Formula	Preparation references	Properties and references
	268	m.p. 225–6°C, i.r. (282)
	329	m.p. 239–40°C
	279, 317, 373	m.p. 217–18°C
	386	m.p. 159–60°C

(z) Polymeric Derivatives

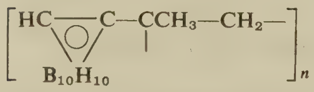
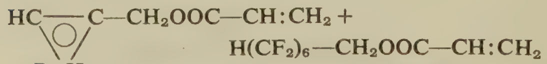
Formula	Preparation references	Properties and references
	481	Mol. wt. 1790 (481)
 copolymer	481	

Table XXVIII.—continued

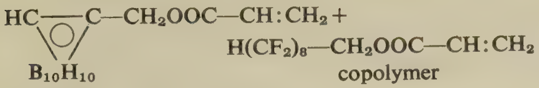
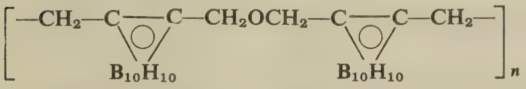
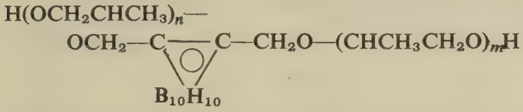
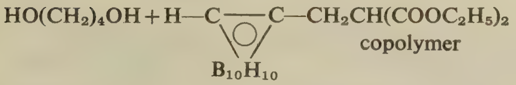
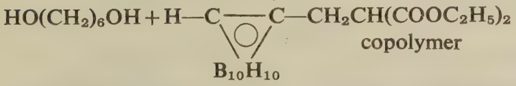
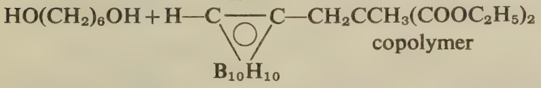
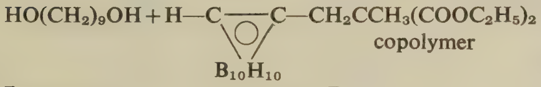
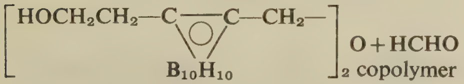
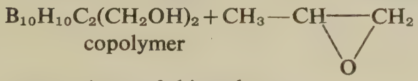
Formula	Preparation references	Properties and references
	481	Mol. wt. 2170, 3000 (2 products, 481)
	475	Mol. wt. 2000 (475)
	480	Mol. wt. 500 (480)
	474	Mol. wt. 1271 (474)
	474	Mol. wt. 1430 (474)
	474	Mol. wt. 2090 (474)
	474	Mol. wt. 1710 (474)
	326	Mol. wt. 2700, i.r. (326)
	479	
Polyurethane of this polymer	479	
$B_{10}H_{10}C_2(CH_2OH)_2 + H_2CO_3$ copolymer	476	Mol. wt. 1100 (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC—COOH$ copolymer	476	Mol. wt. 1160, brittle, softening temp. 72°C (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOCCH_2COOH$ copolymer	476	Mol. wt. 1530, brittle, softening temp. 63°C (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_2COOH$ copolymer	476–7	Mol. wt. 2050, brittle, flow point 90°C (476–7)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_3COOH$ copolymer	474, 476, 480	Mol. wt. 2780, 3600, flow point 63–78°C (474, 476, 480)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_4COOH$ copolymer	474, 476, 480	Mol. wt. 2650, 3060, flow point 61, 80°C (474, 476, 480), rate of formation (478)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_5COOH$ copolymer	476	Mol. wt. 3380 (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_7COOH$ copolymer	474, 476 480	Mol. wt. 2300 (viscous liq.), 3100 (flow point 22°C), 3210, 9500 (474, 476, 480)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CH_2)_8COOH$ copolymer	474, 476, 480	Mol. wt. 2400 (viscous liq.), 3100 (flow point 28°C), 3060 (474, 476, 480)

Table XXVIII.—continued

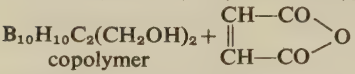
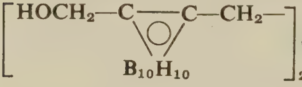
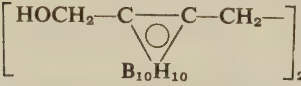
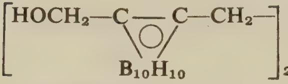
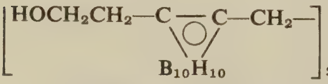
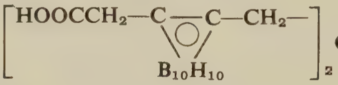
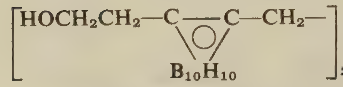
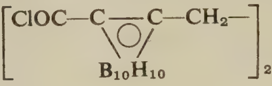
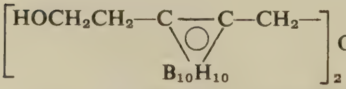
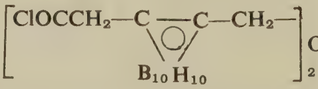
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2(CH_2OH)_2 + ClOC(CH_2)_2COCl$ copolymer	474	Mol. wt. 1907 (vitreous) (474)
$B_{10}H_{10}C_2(CH_2OH)_2 + ClOC(CH_2)_4COCl$ copolymer	474	Mol. wt. 2040 (plastic) (474)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOCCH{:}CHCOOH$ copolymer	476	Mol. wt. 2160 (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC—C_6H_4$-*p*-COOH copolymer	476	Mol. wt. 1410 (476)
$B_{10}H_{10}C_2(CH_2OH)_2 + ClOC—C_6H_4$-*p*-COCl copolymer	474	brittle, softening temp. 270°C (474)
$B_{10}H_{10}C_2(CH_2OH)_2 + (HOOCCH_2)_2O$ copolymer	474	Mol. wt. 2900 (474)
 $B_{10}H_{10}C_2(CH_2OH)_2 + \begin{matrix} CH—CO \\ \Vert \\ CH—CO \end{matrix}\!\!>O$ copolymer	474	
 $\left[HOCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O + HOOC(CH_2)_2COOH$ copolymer	474	Mol. wt. 2800 (brittle, flow point 90°C) (474)
 $\left[HOCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O + HOOC(CH_2)_9COOH$ copolymer	474	Mol. wt. 2650 (viscous liq. at 100°C) (474)
 $\left[HOCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O + ClOC(CH_2)_4COCl$ copolymer	474	Mol. wt. 2300 (brittle, flow point 70°C) (474)
 $\left[HOCH_2CH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O +$  $\left[HOOCCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O$ copolymer	474	Mol. wt. 3250 (474)
 $\left[HOCH_2CH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O +$ $HOOC—CB_{10}H_{10}C—COOH$ copolymer	474	Mol. wt. 1730 (474)
 $HO(CH_2)_4OH + \left[ClOC—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O$ copolymer	474	Mol. wt. 4350 (474)
$B_{10}H_{10}C_2(CH_2OH)_2 + HO(CH_2)_2OH + HOOC(CH_2)_3COOH$ copolymer	475	Mol. wt. 2000 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + HO(CH_2)_2OH + HOOC(CH_2)_4COOH$ copolymer	475	Mol. wt. 2200 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CF_2)_2COOH$ copolymer	475	m.p. 61°C, mol. wt. 2500 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CF_2)_3COOH$ copolymer	475	m.p. 50°C, mol. wt. 3000 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + HOOC(CF_2)_4COOH$ copolymer	475	m.p. 55°C, mol. wt. 3400 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + ClOC(CF_2)_3COCl$ copolymer	474	Mol. wt. 2550 (plastic, flow point 57°C) (474)
 $\left[HOCH_2CH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O + ClOC(CF_2)_3COCl$ copolymer	474	Mol. wt. 1600 (softening temp. 74°C) (474)
 $HOCH_2(CF_2)_3CH_2OH + \left[ClOCCH_2—\underset{B_{10}H_{10}}{C—C}—CH_2—\right]_2 O$ copolymer	474	Mol. wt. 2400 (474)

Table XXVIII.—continued

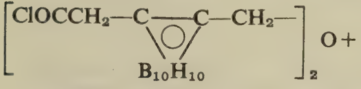
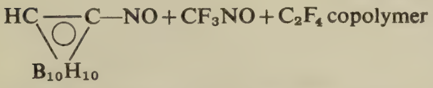
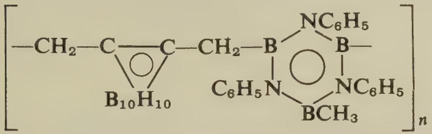
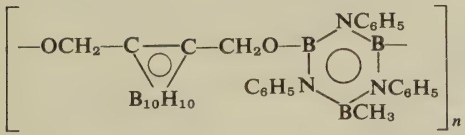
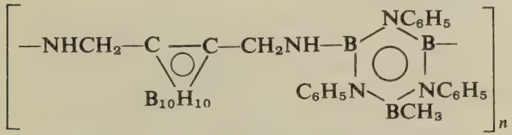
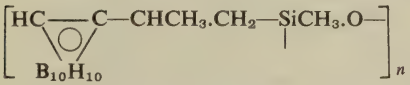
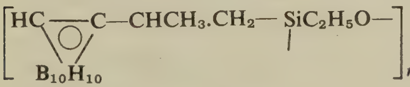
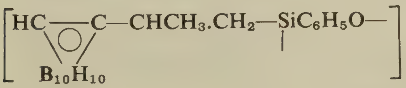
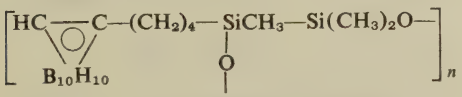
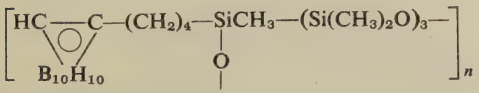
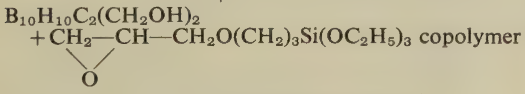
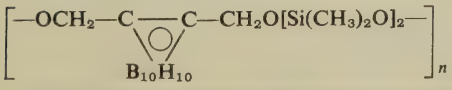
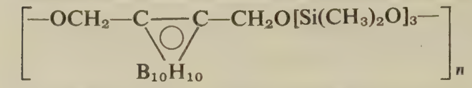
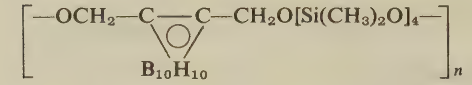
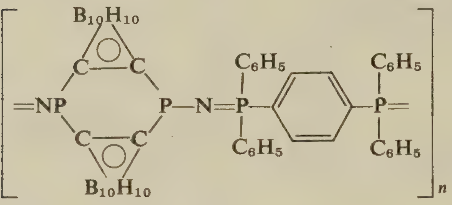
Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2(CH_2OH)_2 + HOCH_2(CF_2)_3CH_2OH +$ $ClOC—C_6H_4—COCl$-*p* copolymer (1:4:5 ratio)	474	Mol. wt. 3300 (474)
 $ClOC—C_6H_4—COCl$-*p* + $HOCH_2(CF_2)_3CH_2OH$ copolymer (1:4:5 ratio)	474	Mol. wt. 2500 (474)
	381	
$B_{10}H_{10}C_2(CH_2OH)_2 + H_3BO_3$ copolymer	475	Mol. wt. 1000 (475)
$B_{10}H_{10}C_2(CH_2OH)_2 + (C_6H_5)_3B_3N_3$ copolymer	475, 482	Mol. wt. 1300 (475, 482)
	482	
	482	
	482	
	485	
	485	
	485	
	319	Mol. wt. 13,000 (319), thermal stability studies (539)
		Thermal stability studies (539)
 $B_{10}H_{10}C_2(CH_2OH)_2 + \underset{O}{CH_2—CH}—CH_2O(CH_2)_3Si(OC_2H_5)_3$ copolymer	484	Polymerization rate (484)
	483	Mol. wt. 580 (483)

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	483	Mol. wt. 900 (483)
	483	Mol. wt. 1170 (483)
	260, 404	

(a′) *B*-substituted Hydrocarbon Derivatives

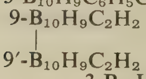
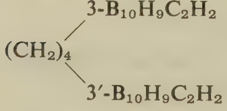
Formula	Preparation references	Properties and references
$B_{10}H_9CH_3C_2H_2$	9	m.p. 140°C
$B_{10}H_8(CH_3)_2C_2H_2$	9	
$B_{10}H_8(CH_3)_2C_2HCH_3$	9	m.p. 153–4°C
3-$B_{10}H_9C_2H_5C_2H_2$	433	m.p. 15–17°C, ^1H n.m.r. (433)
$B_{10}H_9C_2H_5C_2H_2$	9, 30	m.p. −60°C, b.p. 25°C at 4 torr, n_D^{25} 1·5442, d_4^{20} 0·9360, viscosity 2·58 Ns m^{-2} (25·8 P) at 20°C
$B_{10}H_8(C_2H_5)_2C_2H_2$	9	m.p. −27°C, b.p. 65°C at 10 torr, n_D^{25} 1·5352, viscosity 1·30 Ns m^{-2} (13·0 P) at 25°C, ΔH_{comb} 54·5 kJ mol^{-1}
$B_{10}H_7(C_2H_5)_3C_2H_2$	9	b.p. 85–6°C at 0·07 torr, n_D^{30} 1·5267
$B_{10}H_9C_2H_5C_2HCH_3$	9	b.p. 50–4°C at 0·1 torr, n_D^{30} 1·5305
$B_{10}H_8(C_2H_5)_2C_2HCH_3$	9	m.p. −41°C, b.p. 63–4°C at 0·065 torr, n_D^{30} 1·5253, viscosity 1·16 Ns m^{-2} (11·6 P) at 25°C
$B_{10}H_9.C_3H_7.C_2H_2$	9	m.p. −43°C, d_4^{20} 0·9420, viscosity 4·18 Ns m^{-2} (41·8 P) at 20°C
$B_{10}H_8(C_3H_7)_2C_2H_2$	9	
$B_{10}H_7(C_3H_7)_3C_2H_2$	9	
$B_{10}H_9.CH(CH_3)_2C_2H_2$	9	m.p. −45°C, d_4^{20} 0·9360, viscosity 3·47 Ns m^{-2} (34·7 P) at 20°C
$B_{10}H_8[CH(CH_3)_2]_2C_2H_2$	9	
$B_{10}H_7[CH(CH_3)_2]_3C_2H_2$	9	
3-$B_{10}H_9C_6H_5C_2H_2$	433	m.p. 109–10°C, ^1H n.m.r. (433)
$B_{10}H_9C_6H_5C_2H_2$	434	m.p. 108–9°C, ^1H n.m.r. (434), ^{11}B n.m.r. (434)
3:6-$B_{10}H_8(C_6H_5)_2C_2H_2$	433	m.p. 174°C, ^1H n.m.r. (433)
3-$B_{10}H_9C_6H_5C_2(CH_3)_2$	433	m.p. 158–9°C, ^1H n.m.r. (433)
3:6-$B_{10}H_8(C_6H_5)_2C_2(CH_3)_2$	433	m.p. 214–16°C, ^1H n.m.r. (433)
3-$B_{10}H_9C_6H_5C_2HC_6H_5$	433	m.p. 105–6°C, ^1H n.m.r. (433)
 9-$B_{10}H_9C_2H_2$ | 9′-$B_{10}H_9C_2H_2$	442	m.p. 190–1°C
 $(CH_2)_4$(3-$B_{10}H_9C_2H_2$)(3′-$B_{10}H_9C_2H_2$)	435	m.p. 163–4°C

Table XXVIII.—continued

(b′) *B*-substituted Ether, Alcohol, Aldehyde, Carboxylic Acid and Ester Derivatives

Formula	Preparation references	Properties and references
$B_{10}H_9OCH_3.C_2H_2$	439	m.p. 98–9°C
$3\text{-}B_{10}H_9OC_2H_5.C_2H_2$	435	m.p. 38°C
$3\text{-}B_{10}H_9OH.C_2H_2$	437, 448	m.p. 356–8°C
$9\text{-}B_{10}H_9OH.C_2H_2$	439–40	m.p. 412–14°C, i.r. (440)
$3\text{-}B_{10}H_9OH.C_2HCH_3$	437, 448	m.p. 259–61°C
$B_{10}H_9OH.C_2HCH_3$	439–40	m.p. 264–6°C
$9\text{-}B_{10}H_9OH.C_2(CH_3)_2$	439–40	m.p. 292–3°C, i.r. (440)
$3\text{-}B_{10}H_9CHO.C_2H_2$	438	m.p. 242–5°C
$3\text{-}B_{10}H_9COOH.C_2H_2$	438	m.p. 95°C, pK_a 5·38 (438)
$3\text{-}B_{10}H_9OOCCH_3.C_2H_2$	437, 448	m.p. 76–7°C
$3\text{-}B_{10}H_9OOCCH_3.C_2HCH_3$	437, 448	m.p. 74–5°C
$B_{10}H_9OOCCH_3.C_2HCH_3$	439–40	m.p. 141–2°C
$9\text{-}B_{10}H_9ONO_2.C_2H_2$	439–40	m.p. 103–4°C, i.r. (440)
$B_{10}H_9ONO_2.C_2HCH_3$ (isomer a)	439–40	m.p. 99–100°C
$B_{10}H_9ONO_2.C_2HCH_3$ (isomer b)	439–40	m.p. 89–90°C
$9\text{-}B_{10}H_9ONO_2.C_2(CH_3)_2$	439–40	m.p. 68–9°C, i.r. (440)

(c′) *B*-substituted Amine Derivatives

Formula	Preparation references	Properties and references
$3\text{-}B_{10}H_9NH_2.C_2H_2$	436–7	m.p. 218–19°C, pK_a 3·17
$3\text{-}B_{10}H_9NH_2.C_2HCH_3$	436–7	m.p. 231–2°C, pK_a 3·00
$3\text{-}B_{10}H_9NH_2.C_2(CH_3)_2$	436–7	m.p. 319–20°C, pK_a 2·53
$3\text{-}B_{10}H_9NH_2.C_2HC_2H_5$	437	m.p. 91–3°C, pK_a 2·93
$3\text{-}B_{10}H_9NH_2.C_2H[CH(CH_3)_2]$	437	b.p. 116°C at 2 torr, pK_a 2·78
$3\text{-}B_{10}H_9NH_2.C_2HC_6H_5$	436–7	m.p. 81–2°C, pK_a 2·70
$3\text{-}B_{10}H_9NH_2.C_2H_2,HCl$	437, 448	m.p. 290–1°C
$3\text{-}B_{10}H_9NH_2.C_2HCH_3,HCl$	437	m.p. 250–2°C
$3\text{-}B_{10}H_9NH_2.C_2HC_2H_5,HCl$	437	m.p. 220–2°C
$3\text{-}B_{10}H_9NH_2.C_2H[CH(CH_3)_2],HCl$	437	m.p. 215–18°C
$3\text{-}B_{10}H_9N(CH_3)_2.C_2H_2$	437	m.p. 71–2°C
$3\text{-}B_{10}H_9N(CH_3)_2.C_2HCH_3$	437	m.p. 61–3°C
$3\text{-}B_{10}H_9N(C_2H_5)_2C_2H_2$	435, 437	m.p. 84–5°C
$3\text{-}B_{10}H_9NC_5H_{10}.C_2H_2$	437	m.p. 62°C
$3\text{-}B_{10}H_9N(C_6H_5)_2C_2H_2$	432	
$3\text{-}B_{10}H_9NHCONHC_6H_5.C_2H_2$	437	m.p. 151–3°C
$3\text{-}B_{10}H_9NHCONHC_6H_5.C_2HCH_3$	437	m.p. 160–2°C
$3\text{-}B_{10}H_9NHOCCH_3.C_2H_2$	437, 448	m.p. 129–30°C
$3\text{-}B_{10}H_9NHOCCH_3.C_2HCH_3$	437	m.p. 150–1°C
$3\text{-}B_{10}H_9NHOCC_6H_5.C_2H_2$	437	m.p. 179–80°C
$3\text{-}B_{10}H_9NHOCC_6H_5.C_2HCH_3$	437	m.p. 170–1°C

(d′) *B*-substituted Fluorine Derivatives

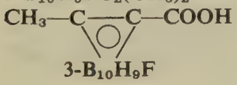
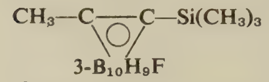
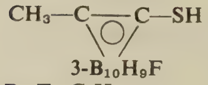
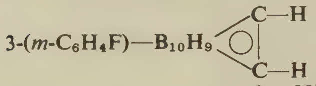
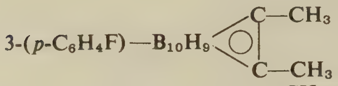
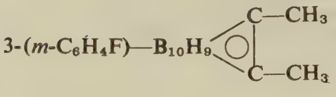
Formula	Preparation references	Properties and references
$3\text{-}B_{10}H_9FC_2H_2$	9, 432, 437, 446	m.p. 242°C
$3\text{-}B_{10}H_9FC_2HCH_3$	437, 446	m.p. 207–8°C
$3\text{-}B_{10}H_9FC_2(CH_3)_2$	437, 446	m.p. 234–5°C
 $\underset{3\text{-}B_{10}H_9F}{CH_3\text{—}C\text{——}C\text{—}COOH}$	437, 446	m.p. 240°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	437	m.p. 98°C
	437	m.p. 241°C
$B_{10}F_{10}C_2H_2$	317, 428	m.p. 258–60°C
	281	m.p. 64–5°C, ^{19}F n.m.r. (281)
	281	m.p. 155–6°C, ^{19}F n.m.r. (281)
	281	m.p. 108–9°C, ^{19}F n.m.r. (281)

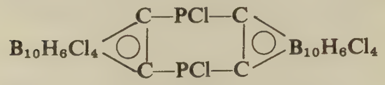
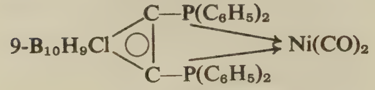
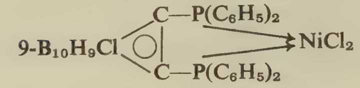
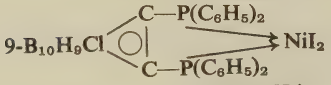
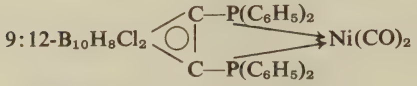
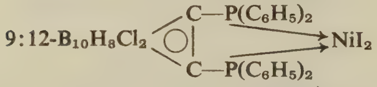
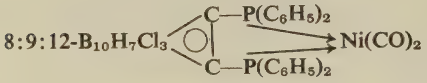
(e′) *B*-substituted Chlorine Derivatives

Formula	Preparation references	Properties and references
$3\text{-}B_{10}H_9ClC_2H_2$	437, 448	m.p. 169–70°C
$9\text{-}B_{10}H_9ClC_2H_2$	292, 429, 447, 462	m.p. 237–8°C, i.r. (282), μ 19·8 × 10^{-30} C m (5·93 D) (293, 451), ^{35}Cl n.q.r. (416)
$B_{10}H_9ClC_2H_2$	449	m.p. 224–5°C, i.r. (449)
$7{:}9\text{-}B_{10}H_8Cl_2C_2H_2$	463	m.p. 165–6°C
$9{:}10\text{-}B_{10}H_8Cl_2C_2H_2$	185, 447	m.p. 220–1°C
$9{:}12\text{-}B_{10}H_8Cl_2C_2H_2$	449	m.p. 264–5°C, ^{35}Cl n.q.r. (416), μ 23·3 × 10^{-30} C m (6·98 D) (293, 451)
$B_{10}H_8Cl_2C_2H_2$	185	m.p. 250–1°C
$B_{10}H_7Cl_3C_2H_2$	185, 447	m.p. 241–3°C
$B_{10}H_7Cl_3C_2H_2$	463	m.p. 256–7°C
$B_{10}H_7Cl_3C_2H_2$	449	m.p. 314–15°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Cl_4C_2H_2$	185, 292, 429, 449	m.p. 352–3°C, ^{35}Cl n.q.r. (416)
$B_{10}H_6Cl_4C_2H_2$ (isomer a)	185, 447	m.p. 227–8°C, ^{35}Cl n.q.r. (416)
$B_{10}H_6Cl_4C_2H_2$ (isomer b)	352	m.p. 323–4°C
$B_{10}H_5Cl_5C_2H_2$ (isomer a)	292	m.p. 324–5°C
$B_{10}H_5Cl_5C_2H_2$ (isomer b)	352, 449	m.p. 296–8°C, i.r. (449)
$B_{10}H_4Cl_6C_2H_2$	185	m.p. 306°C
$3{:}6\text{-}B_{10}H_2Cl_8C_2H_2$	185	m.p. 272–3°C, i.r. (185), ^{35}Cl n.q.r. (416), *X*-ray (243, 244)
$B_{10}Cl_{10}C_2H_2$	185, 352, 449	m.p. 263–4°C, pK_a 6·89 (444), i.r. (185, 282, 449), ^{1}H n.m.r. (185, 241, 360), ^{35}Cl n.q.r. (416), ^{11}B n.m.r. (185, 241, 360), μ 21·2 × 10^{-30} C m (6·36 D) (293, 451)
$B_{10}Cl_{10}C_2HCl$	185, 449	m.p. 279, 426–30°C decomp., i.r. (185, 449), ^{1}H n.m.r. (185), ^{11}B n.m.r. (185)
$B_{10}Cl_{10}C_2Cl_2$	352, 360, 444	m.p. 422–4°C decomp., ^{11}B n.m.r. (360), i.r. (282, 360)
$B_{10}Cl_{10}C_2D_2$	443	

Table XXVIII.—continued

Formula	Preparation references	Properties and references
$B_{10}H_9ClC_2HCl$	359, 380	m.p. 178–9°C, ^{35}Cl n.q.r. (416), μ 10·8–11·0 × 10^{-30} C m (3·25–3·31 D) (294)
$B_{10}H_9ClC_2HCl$	380	m.p. 209–11°C, μ 11·5–11·8 × 10^{-30} C m (3·45–3·54 D) (294)
$B_{10}H_8Cl_2C_2HCl$	380	m.p. 127–9°C
$B_{10}H_8Cl_2C_2HCl$	380	m.p. 145–9°C
3-$B_{10}H_9ClC_2HCH_3$	437, 448	m.p. 184–5°C
9-$B_{10}H_9ClC_2HCH_3$	292, 447	m.p. 156°C
12-$B_{10}H_9ClC_2HCH_3$	292, 445	m.p. 142–3°C
8:9-$B_{10}H_8Cl_2C_2HCH_3$	463	
8:12-$B_{10}H_8Cl_2C_2HCH_3$	463	
9:12-$B_{10}H_8Cl_2C_2HCH_3$	292, 447, 463	m.p. 151–2°C
$B_{10}H_8Cl_2C_2HCH_3$	449	m.p. 150–1°C
$B_{10}H_7Cl_3C_2HCH_3$	447, 449	m.p. 176–7°C
8:9:10:12-$B_{10}H_6Cl_4C_2HCH_3$	292	m.p. 223–4°C
$B_{10}H_5Cl_5C_2HCH_3$	358	m.p. 236–8°C
$B_{10}H_3Cl_7C_2HCH_3$	449	m.p. 262–4°C
$B_{10}Cl_{10}C_2HCH_3$	360	pK_a 6·90 (444), ^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
9:12-$B_{10}H_8Cl_2C_2(CH_3)_2$	447	m.p. 118–19°C
$B_{10}Cl_{10}C_2(CH_3)_2$	360–1	m.p. > 400°C, i.r. (361), ^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
$B_{10}Cl_{10}C_2CH_3.C_2H_5$	361	m.p. > 400°C
9-$B_{10}H_9ClC_2CH_3Cl$	358	m.p. 149–50°C
12-$B_{10}H_9ClC_2CH_3Cl$	358	
$B_{10}H_9ClC_2CH_3Cl$	358–9, 380	m.p. 222–4°C, μ 12·4–12·6 × 10^{-30} C m (3·72–3·78 D) (294)
9:12-$B_{10}H_8Cl_2C_2H.CH_2Cl$		^{35}Cl n.q.r. (416)
8:9:10:12-$B_{10}H_6Cl_4C_2H.CH_2Cl$		^{35}Cl n.q.r. (416)
$B_{10}H_5Cl_5C_2H.CH_2Cl$	449	m.p. 172–3°C
$B_{10}Cl_{10}C_2HC_2H_5$	360–1	m.p. > 400°C, i.r. (361), ^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
$B_{10}Cl_{10}C_2(C_2H_5)_2$	360	^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
9:12-$B_{10}H_8Cl_2C_2H.CH{:}CH_2$	320	m.p. 81–2°C, ^{35}C n.q.r. (416)
$B_{10}H_7Cl_3C_2H.CH{:}CH_2$	320	m.p. 105–6°C
$B_{10}Cl_{10}C_2H.CH_2CH{:}CH_2$	361	m.p. 330–2°C decomp.
$B_{10}Cl_{10}C_2.CH_2CH{:}CH_2)_2$	361	m.p. 422–4°C decomp.
8-$B_{10}H_9ClC_2HC_6H_5$	314–15, 463	m.p. 70–1°C
9-$B_{10}H_9ClC_2HC_6H_5$	292, 429, 430, 463	m.p. 63–4°C
12-$B_{10}H_9ClC_2HC_6H_5$	292, 314–15 429–30, 463	m.p. 85–6°C
9:12-$B_{10}H_8Cl_2C_2HC_6H_5$	445	m.p. 99°C
$B_{10}H_8Cl_2C_2HC_6H_5$	449	m.p. 50–1°C
$B_{10}H_2Cl_8C_2HC_6H_5$	352, 449	m.p. 216–18°C
$B_{10}Cl_{10}C_2HC_6H_5$	352, 449	m.p. 240–1°C
$B_{10}Cl_{10}C_2H.CH_2C_6H_5$	361	m.p. 182–3°C
$B_{10}Cl_{10}C_2(CH_2C_6H_5)_2$	361	m.p. 216–17°C
$B_{10}H_7Cl_3C_2H.C_6H_3Cl_2$	449	m.p. 170–2°C
8:9:10:12-$B_{10}H_6Cl_4C_2H.C_6Cl_5$	292, 429, 430	m.p. 231–2°C
9:12-$B_{10}H_8ClBrC_2H_2$	292, 429	m.p. 238–9°C
$B_{10}Cl_{10}C_2Br_2$	444	m.p. 341–4°C decomp., i.r. (282)
$B_{10}Cl_8Br_2C_2H_2$	427	m.p. 301–2°C, pK_a 6·95 (444)
$B_{10}H_2Cl_5Br_3C_2H_2$	427	m.p. 346–8°C
$B_{10}H_6ClI_3C_2H_2$	445	m.p. 299–301°C
(9:12-$B_{10}H_8Cl_2C_2H$—$)_2Hg$	391	m.p. 308–10°C decomp., polarography (391)
9:12-$B_{10}H_8Cl_2C_2CH_3.HgCH_3$	389	m.p. 265°C
9-$B_{10}H_9ClC_2[P(C_6H_5)_2]_2$	402	m.p. 201–3°C
9:12-$B_{10}H_8Cl_2C_2[P(C_6H_5)_2]_2$	402	m.p. 228–30°C
8:9:12-$B_{10}H_7Cl_3C_2[P(C_6H_5)_2]_2$	402	m.p. 215–17°C

Table XXVIII.—continued

Formula	Preparation references	Properties and references
	363	m.p. 426–7°C
	402	m.p. 206°C decomp.
	402	m.p. 250°C decomp.
	402	
	402	m.p. 222–4°C
	402	
	402	m.p. 200°C decomp.

(f′) *B*-substituted Bromine Derivatives

Formula	Preparation references	Properties and references
$3\text{-}B_{10}H_9BrC_2H_2$	9, 432, 437, 448, 466	m.p. 118–19°C
$4\text{-}B_{10}H_9BrC_2H_2$	466	optical resolution (547)
$8\text{-}B_{10}H_9BrC_2H_2$	314–15, 466	m.p. 186–7°C, i.r. (282)
$9\text{-}B_{10}H_9BrC_2H_2$	363, 418, 449, 466	m.p. 192°C, μ 19·7 × 10^{-30} C m (5·90 D) (293, 451), *X*-ray (249), i.r. (282), ^{1}H n.m.r. (249)
$B_{10}H_9BrC_2H_2$	449	m.p. 185–6°C
$8{:}9\text{-}B_{10}H_8Br_2C_2H_2$	314–15	m.p. 202–3°C
$9{:}12\text{-}B_{10}H_8Br_2C_2H_2$	363, 418, 447, 449	m.p. 187–8 or 226–7°C, i.r. (282), ^{11}B n.m.r. (249), *X*-ray (249–50), μ 23·9–24·0 × 10^{-30} C m (7·18–7·21 D) (291, 293, 451)
$B_{10}H_8Br_2C_2H_2$	447	m.p. 149–50°C
$8{:}9{:}12\text{-}B_{10}H_7Br_3C_2H_2$	94, 315, 363	m.p. 329°C, i.r. (282), ^{11}B n.m.r. (249), *X*-ray (249, 251)
$B_{10}H_7Br_3C_2H_2$	447	m.p. 268–9°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2H_2$	447, 449	m.p. 344–5°C, i.r. (282)
$B_{10}H_6Br_4C_2H_2$	447	m.p. 324–5°C
$B_{10}H_4Br_6C_2H_2$	447	m.p. 314–15°C
$8\text{-}B_{10}H_9BrC_2HCH_3$	315	m.p. 120–1°C
$9\text{-}B_{10}H_9BrC_2HCH_3$	292, 447	m.p. 102–3 or 128–9°C
$12\text{-}B_{10}H_9BrC_2HCH_3$	292, 314–15	m.p. 167–8°C
$8{:}9\text{-}B_{10}H_8Br_2C_2HCH_3$	314–15	m.p. 110–11°C
$8{:}12\text{-}B_{10}H_8Br_2C_2HCH_3$	314–15, 449	m.p. 154–5°C
$9{:}12\text{-}B_{10}H_8Br_2C_2HCH_3$	292, 449	m.p. 119–20 or 149–50°C

Table XXVIII.—continued

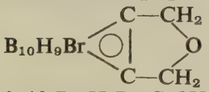
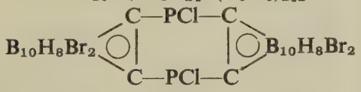
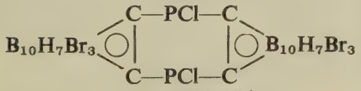
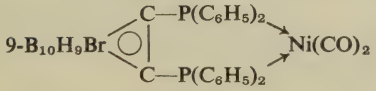
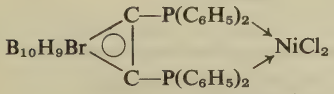
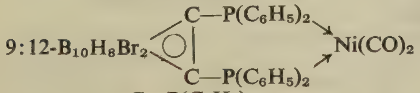
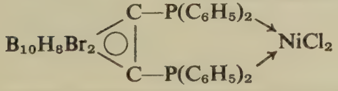
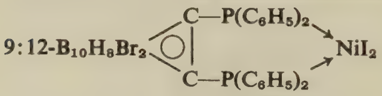
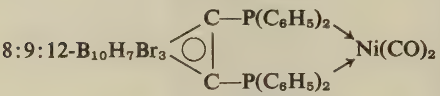
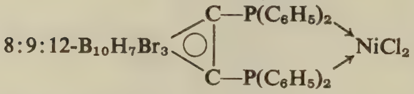
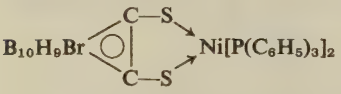
Formula	Preparation references	Properties and references
$B_{10}H_8Br_2C_2HCH_3$ (isomer a)	286	m.p. 154°C
$B_{10}H_8Br_2C_2HCH_3$ (isomer b)	286	m.p. 96–7°C
$8{:}9{:}12\text{-}B_{10}H_7Br_3C_2HCH_3$	292, 314–15	m.p. 169–70°C
$B_{10}H_7Br_3C_2HCH_3$	447	m.p. 203–5°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2HCH_3$	292	m.p. 224–5°C
$B_{10}H_5Br_5C_2HCH_3$	447	m.p. 252–3°C
$B_{10}H_9BrC_2(CH_3)_2$	363, 418	m.p. 133°C
$B_{10}H_8Br_2C_2(CH_3)_2$	363	m.p. 256–7°C
$B_{10}H_7Br_3C_2(CH_3)_2$	363	m.p. 265–7°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2(CH_3)_2$	363	m.p. 330–2°C ^{11}B n.m.r. (249), *X*-ray (249, 252)
$9{:}12\text{-}B_{10}H_8Br_2C_2H.CH_2Br$	292	m.p. 129–30°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2H.CH{:}CH_2$	320	m.p. 196–7°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2H.CHBrCH_2Br$	320	m.p. 169°C
$8\text{-}B_{10}H_9BrC_2HC_6H_5$	314–15	m.p. 87–8°C
$9\text{-}B_{10}H_9BrC_2HC_6H_5$	292	m.p. 70–1°C
$12\text{-}B_{10}H_9BrC_2HC_6H_5$	292, 463	m.p. 105–6°C
$B_{10}H_9BrC_2HC_6H_5$	449	m.p. 72–3°C
$8{:}9\text{-}B_{10}H_8Br_2C_2HC_6H_5$	315	m.p. 75–6°C
$8{:}12\text{-}B_{10}H_8Br_2C_2HC_6H_5$	315	m.p. 108–9°C
$9{:}12\text{-}B_{10}H_8Br_2C_2HC_6H_5$	292, 449	m.p. 118–19°C
$9\text{-}B_{10}H_9BrC_2(C_6H_5)_2$	429	m.p. 128–9°C
$B_{10}H_6Br_4C_2H.C_6H_3Br_2$	449	m.p. 174–5°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2H.C_6H_2Br_3$	292, 430	m.p. 243–4°C
$9{:}12\text{-}B_{10}H_8ClBrC_2H_2$	292, 429	m.p. 238–9°C
$B_{10}Cl_8Br_2C_2H_2$	427	m.p. 301–2°C, pK_a 6·95 (444)
$B_{10}H_2Cl_5Br_2C_2H_2$	427	m.p. 346–8°C
	9, 186, 240	m.p. 127–9°C
$9{:}12\text{-}B_{10}H_8Br_2C_2CH_3.HgCH_3$	389	m.p. 263°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2CH_3.HgCH_3$	389	m.p. 322°C
$8{:}9{:}10{:}12\text{-}B_{10}H_6Br_4C_2CH_3.HgC_6H_5$	389	m.p. 254°C
$9\text{-}B_{10}H_9BrC_2[P(C_6H_5)_2]_2$	363	m.p. 217–19°C
$9{:}12\text{-}B_{10}H_8Br_2C_2[P(C_6H_5)_2]_2$	363	m.p. 235–7°C
$9{:}12\text{-}B_{10}H_8Br_2C_2[P(C_6H_5)_2]_2$	363	m.p. 199–200°C
$9{:}12\text{-}B_{10}H_8Br_2C_2[P(C_6H_5)N_3]_2$	363	m.p. 125°C decomp.
$8{:}9{:}12\text{-}B_{10}H_7Br_3C_2[P(C_6H_5)_2]_2$	363	m.p. 236–8°C
	363	m.p. 415°C
	363	m.p. 412–14°C
	402	m.p. 198–9°C
	405	u.v. (405), conductivity (405)
	402	m.p. 235°C decomp.
	405	u.v. (405), conductivity (405)

Table XXVIII.—*continued*

Formula	Preparation references	Properties and references
	402	
	402	m.p. 240°C decomp.
	402, 405	m.p. 245°C decomp., u.v. (405), conductivity (405)
$B_{10}H_9BrC_2(SH)_2$	409	m.p. 138–40°C
$B_{10}H_7Br_3C_2(SH)_2$	409	m.p. 203–6°C
$B_{10}H_8Br_2C_2(SCH_3)_2$	409	m.p. 181–3°C
$B_{10}H_8Br_2C_2(SC_2H_5)_2$	409	m.p. 95–7°C
	407	

(g′) *B*-substituted Iodine Derivatives

Formula	Preparation references	Properties and references
9-$B_{10}H_9IC_2H_2$	9, 292, 418, 429, 447	m.p. 122–3°C, μ 19·7 × 10^{-30} C m (5·96 D) (293, 451), i.r. (282)
9:12-$B_{10}H_8I_2C_2H_2$	292, 418, 429	m.p. 194–5°C, μ 23·4 × 10^{-30} C m (7·02 D) (293, 451)
8:9:12-$B_{10}H_7I_3C_2H_2$	418, 449	m.p. 291–2°C
8:9:10:12-$B_{10}H_6I_4C_2H_2$	449	m.p. 324–5°C
$B_{10}H_9{}^{131}IC_2H_2$	441	
$B_{10}H_8{}^{131}I_2C_2H_2$	441	
9-$B_{10}H_9IC_2HCH_3$	292, 429	m.p. 129–30°C
12-$B_{10}H_9IC_2HCH_3$	292, 429	m.p. 157–8°C
9:12-$B_{10}H_8I_2C_2HCH_3$	292, 429	m.p. 158–9°C
$B_{10}H_8I_2C_2HCH_3$	447	m.p. 128–9°C
9-$B_{10}H_9IC_2H.CH{:}CH_2$	320	m.p. 68–9°C
12-$B_{10}H_9IC_2H.CH{:}CH_2$	320	m.p. 148–9°C
9:12-$B_{10}H_8I_2C_2H.CH{:}CH_2$	320	m.p. 153–4°C
8:9:12-$B_{10}H_7I_3C_2H.CH{:}CH_2$	320	m.p. 154–5°C
8:9:10:12-$B_{10}H_6I_4C_2H.CH{:}CH_2$	320	m.p. 183–4°C
8-$B_{10}H_9IC_2HC_6H_5$	314–15	m.p. 127–8°C
9-$B_{10}H_9IC_2HC_6H_5$	292, 315, 429	m.p. 94–5°C
12-$B_{10}H_9IC_2HC_6H_5$	253, 292, 314–15, 429, 449	m.p. 146–7°C, *X*-ray (253)
9:12-$B_{10}H_8I_2C_2HC_6H_5$	430	m.p. 121–2°C
$B_{10}H_6ClI_3C_2H_2$	445	m.p. 299–301°C

(h′) Lewis Base Adducts

Formula	Preparation references	Properties and references
$B_{10}H_{10}C_2H_2,2N(C_3H_7)_3$	186	
$B_{10}H_{10}C_2H_2,2NC_5H_{10}$	186	m.p. 171–6°C
$B_{10}H_{10}C_2HCH_3,2N(C_3H_7)_3$	186	
$B_{10}H_{10}C_2H.CH_2Br,2(CH_2)_6N_4$	186	
$B_{10}H_{10}C_2(COOCH_3)_2,2N[CH(CH_3)_2]_3$	186	
$B_{10}H_2Cl_8C_2H_2,2N(C_2H_5)_3$	185	

Table XXVIII.—continued

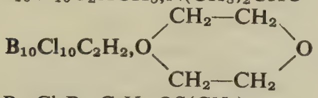
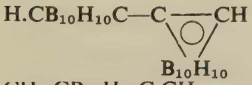
Formula	Preparation references	Properties and references
$B_{10}Cl_{10}C_2H_2,N(CH_3)_3$	444	m.p. 150–60°C decomp.
$B_{10}Cl_{10}C_2H_2,N(C_2H_5)_3$	444	m.p. 165–6°C
$B_{10}Cl_{10}C_2HCH_3,N(CH_3)_3$	444	m.p. 170–90°C decomp.
$B_{10}Cl_{10}C_2HCH_3,N(C_2H_5)_3$	444	m.p. 120–40°C decomp.
$B_{10}Cl_{10}C_2HC_2H_5,N(C_2H_5)_3$	444	m.p. 146°C decomp.
$B_{10}Cl_{10}C_2HCl,N(C_2H_5)_3$	185	
$B_{10}Cl_{10}C_2CH_3Cl,P(C_6H_5)_3$	185	
$B_{10}Cl_{10}C_2H_2,2N(C_2H_5)_3$	185	
$B_{10}Cl_{10}C_2H_2,OS(CH_3)_2$	444	m.p. 159–60°C, i.r. (443)
$B_{10}Cl_{10}C_2HCH_3,OS(CH_3)_2$	444	m.p. 150–1°C decomp., i.r. (443)
$B_{10}Cl_{10}C_2HC_2H_5,OS(CH_3)_2$	444	m.p. 158°C decomp., i.r. (443)
$B_{10}Cl_{10}C_2H_2,N(CH_3)_2CHO$	444	m.p. 151–4°C decomp., i.r. (443)
$B_{10}Cl_{10}C_2HCH_3,N(CH_3)_2CHO$	444	m.p. 145–51°C decomp., i.r. (443)
	443	m.p. 190–205°C
$B_{10}Cl_8Br_2C_2H_2,OS(CH_3)_2$	444	m.p. 176°C decomp., i.r. (443)

Table XXIX.—Derivatives of Closo-1:7-*dicarbadodecaborane*(12)

(a) *C*-hydrocarbon Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.CH_3$	9, 81, 109, 304, 351, 371	m.p. 208–10°C, i.r. (282)
$H.CB_{10}H_{10}C.C_6H_5$	166, 304, 324, 351, 373	m.p. 55–6°C
	268	m.p. 225–6°C, i.r. (282)
$CH_3.CB_{10}H_{10}C.CH_3$	79, 111, 371	m.p. 170°C
$CH_3.CB_{10}H_{10}C—CH:CH_2$	329	m.p. 75–6°C
$CH_3.CB_{10}H_{10}C—CH:CHCH_3$	329	
$CH_3.CB_{10}H_{10}C.C_6H_5$	351, 371	m.p. 58–9°C
$C_3H_7.CB_{10}H_{10}C.C_3H_7$	371	m.p. 47–8°C
$CH_2:CCH_3.CB_{10}H_{10}C.CCH_3:CH_2$	452	m.p. 46–7°C, b.p. 85–91°C at 1 torr
$C_6H_5.CB_{10}H_{10}CC_6H_5$	268	m.p. 116–17°C
$C_6H_5CH_2.CB_{10}H_{10}C.CH_2C_6H_5$	351	m.p. 79–80°C
$C_6H_5.CB_{10}H_{10}C—C_6H_4\text{-}p\text{-}C_6H_5$	373	m.p. 58–9°C

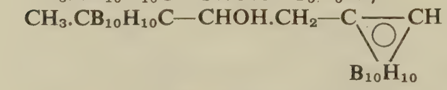
(b) *C*-halogen Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.Br$	282	i.r. (282)
$H.CB_{10}H_{10}C.I$	304	
$F.CB_{10}H_{10}C.F$	431	m.p. 230–1°C, i.r. (431)
$Cl.CB_{10}H_{10}C.Cl$	282	i.r. (282)
$Br.CB_{10}H_{10}C.Br$	280	m.p. 118–20°C, i.r. (282), μ 5·47 × 10^{-30} C m (1·64 D) (291)

Table XXIX.—continued

Formula	Preparation references	Properties and references
$I.CB_{10}H_{10}C.I$	280	m.p. 74–5°C
$CH_3.CB_{10}H_{10}C.Cl$	280	m.p. 169–70°C
$CH_3.CB_{10}H_{10}C.Br$	280	m.p. 147–8°C
$CH_3CB_{10}H_{10}C.I$	280	m.p. 71–2°C
$C_6H_5.CB_{10}H_{10}C.I$	373	m.p. 86–7°C
$H.CB_{10}H_{10}C{—}C_6H_4F\text{-}p$	281, 310	m.p. 62–3°C, ^{19}F n.m.r. (281, 310)
$H.CB_{10}H_{10}C{—}C_6H_4F\text{-}m$	281, 310	m.p. 46–7°C, ^{19}F n.m.r. (281, 310)
$H.CB_{10}H_{10}C{—}C_6H_4Cl\text{-}p$	324	m.p. 61–2°C
$H.CB_{10}H_{10}C{—}C_6H_4Br\text{-}p$	324	m.p. 71–2°C
$H.CB_{10}H_{10}C{—}C_6H_4I\text{-}p$	324	m.p. 77–8°C
$H.CB_{10}H_{10}C.CCH_3.CF_3.OH$	452	b.p. 120–4°C at 1–2 torr
$H.CB_{10}H_{10}C.C(CF_3)_2OH$	452	m.p. 80–1°C
$H.CB_{10}H_{10}C.CCF_3.CF_2Cl.OH$	452	m.p. 43–5°C, b.p. 140–5°C at 1–2 torr
$CH_3.CB_{10}H_{10}C{—}C_6H_4F\text{-}p$	281	m.p. 44°C, ^{19}F n.m.r. (281)
$CH_3.CB_{10}H_{10}C{—}C_6H_4F\text{-}m$	281	b.p. 147–9°C at 5 torr, ^{19}F n.m.r. (281)
$CH_3.CB_{10}H_{10}C.COCH_2Br$	337	b.p. 98–102°C at 3 torr, i.r. (337), n_D^{25} 1·5566, ^1H n.m.r. (337)
$[OC(CF_3)_2CB_{10}H_{10}C.C(CF_3)_2O]^{2-}$	452	$(CH_3)_2NH_2^+$ salt: m.p. 105–6°C

(c) *C*-alcohol Derivatives

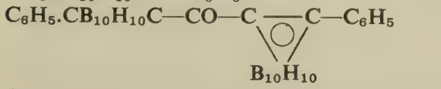
Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.C(CH_3)_2OH$	452	m.p. 122–3°C
$H.CB_{10}H_{10}C.CCH_3.CF_3.OH$	452	b.p. 120–4°C at 1–2 torr
$H.CB_{10}H_{10}C.C(CF_3)_2OH$	452	m.p. 80–1°C
$H.CB_{10}H_{10}C.CCF_3.CF_2Cl.OH$	452	m.p. 43–5°C, b.p. 140–5°C at 1–2 torr
$CH_3.CB_{10}H_{10}C.CH_2OH$	371	m.p. 181–2°C
$CH_3.CB_{10}H_{10}C.CHOH.CH_3$	328	m.p. 42–3°C
$CH_3.CB_{10}H_{10}C.C(CH_3)_2OH$	329	m.p. 29–30°C, ^1H n.m.r. (329)
$CH_3.CB_{10}H_{10}C.CHC_6H_5.OH$	329	b.p. 152–3°C at 1·5 torr, n_D^{20} 1·5807
$CH_3.CB_{10}H_{10}C.C(C_6H_5)_2OH$	329	m.p. 90–1°C, ^1H n.m.r. (329)
$CH_3.CB_{10}H_{10}C{—}CHOH{—}C_5H_5N\text{-}\gamma$	371	m.p. 208–9°C
 $CH_3.CB_{10}H_{10}C{—}CHOH.CH_2{—}\underset{B_{10}H_{10}}{C{—}CH}$	329	m.p. 239–40°C
$C_6H_5.CB_{10}H_{10}C{—}CHOH{—}C_6H_4OCH_3\text{-}p$	371	m.p. 102–3°C
$HOCH_2CB_{10}H_{10}C.CH_2OH$	81	m.p. 194–6°C
$HOCHCH_3.CB_{10}H_{10}C{—}CHOH.CH_3$	371	m.p. 106–7°C
$HOCHC_6H_5.CB_{10}H_{10}C{—}CHOHC_6H_5$	371	m.p. 96–7°C

(d) *C*-ether Derivatives

Formula	Preparation references	Properties and references
$C_6H_5CB_{10}H_{10}C{—}CHOH{—}C_6H_4OCH_3\text{-}p$	371	m.p. 102–3°C
$C_6H_5.CB_{10}H_{10}C{—}CO{—}C_6H_4OCH_3\text{-}p$	371	m.p. 85–6°C

Table XXIX.—continued

(e) *C*-aldehyde and *C*-ketone Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.CHO$	327, 331, 333	m.p. 213–14°C, i.r. (331)
$CH_3.CB_{10}H_{10}C.CHO$	329	m.p. 143–4°C
$CH_3.CB_{10}H_{10}C.CH_2CHO$	329	b.p. 98°C at 2 torr
$CH_3.CB_{10}H_{10}C.COMe$	328	b.p. 78–80°C at 3 torr, n_D^{25} 1·5247, i.r. (337), ^1H n.m.r. (337)
$CH_3.CB_{10}H_{10}C.COCH_2Br$	337	b.p. 98–102°C at 3 torr, n_D^{25} 1·5566, i.r. (337), ^1H n.m.r. (337)
$CH_3CB_{10}H_{10}C.COC_6H_5$	337	polarography (337)
 $C_6H_5.CB_{10}H_{10}C{-}CO{-}\underset{B_{10}H_{10}}{C{-}C}{-}C_6H_5$	279, 317, 373	m.p. 217–18°C
$C_6H_5.CB_{10}H_{10}C{-}CHC_6H_5CH_2COC(CH_3)_3$	371	m.p. 77–8°C
$C_6H_5.CB_{10}H_{10}C{-}CO{-}C_6H_4OCH_3\text{-}p$	371	m.p. 85–6°C
$CH_3CO.CB_{10}H_{10}C.COCH_3$	371	m.p. 70–1°C
$C_6H_5CO.CB_{10}H_{10}C.COC_6H_5$	371	m.p. 57–8°C

(f) *C*-carboxylic Acid Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.COOH$	342, 355	m.p. 163–5°C, i.r. (342)
$H.CB_{10}H_{10}C{-}{}^{14}COOH$	339	
$H.CB_{10}H_{10}C{-}C_6H_4.COOH\text{-}m$	310	m.p. 280–1°C, pK_a 5·84
$CH_3.CB_{10}H_{10}C.COOH$	81	m.p. 108–11°C
$CH_3.CB_{10}H_{10}C.CH_2COOH$	327	m.p. 118–20°C
$C_6H_5.CB_{10}H_{10}C.COOH$	373	m.p. 120–1°C
$HOOC.CB_{10}H_{10}C.COOH$	81	m.p. 202–4°C

(g) *C*-ester and Other Carboxylic Acid Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.COOCH_3$	342	
$C_6H_5.CB_{10}H_{10}C.COOC_2H_5$	373	
$CH_3OOC.CB_{10}H_{10}C.COOCH_3$	81	m.p. 52–4°C
$CH_3COOC(CH_3)_2.CB_{10}H_{10}C.C(CH_3)_2OOCCH_3$	452	m.p. 64–5°C
$C_6H_5.CB_{10}H_{10}C.COCl$	373	b.p. 157–9°C at 4·0 torr
$ClCO.CB_{10}H_{10}C.COCl$	376	
$C_6H_5.CB_{10}H_{10}C.CONH_2$	373	m.p. 125–6°C
$H_2NCO.CB_{10}H_{10}C.CONH_2$	376	m.p. 183°C
$H.CB_{10}H_{10}C{-}C_6H_4.NHCOCH_3\text{-}p$	324	m.p. 159–60°C

(h) *C*-nitrogen Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.NH_2$	346	m.p. 290–1°C
$H.CB_{10}H_{10}C{-}C_6H_4.NH_2\text{-}p$	324	m.p. 111–12°C
$C_6H_5.CB_{10}H_{10}C.NH_2$	346	m.p. 87–8°C
$H.CB_{10}H_{10}C{-}C_6H_4.NO_2\text{-}p$	174	m.p. 148–9°C
$H.CB_{10}H_{10}C{-}C_6H_4\text{-}p{-}N{=}N{-}C_{10}H_7.OH{-}\alpha$	324	
$H.CB_{10}H_{10}C.CON_3$	346	m.p. 69–70°C
$C_6H_5.CB_{10}H_{10}C.CON_3$	346	m.p. 51–2°C
$C_6H_5.CB_{10}H_{10}C.CONC_6H_5$	371	m.p. 121–2°C
$C_6H_5.CB_{10}H_{10}C.CSNC_6H_5$	371	m.p. 136–7°C
$CH_3.CB_{10}H_{10}C{-}CHOH{-}C_6H_4N\text{-}\gamma$	371	m.p. 208–9°C

Table XXIX.—continued

(i) *C*-silicon Derivatives

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C.Si(CH_3)_3$	282	m.p. 63–4°C, i.r. (282)
$(CH_3)_3Si.CB_{10}H_{10}C.Si(CH_3)_3$	397	
$(CH_3)_2C_6H_5Si.CB_{10}H_{10}C.Si(CH_3)_2C_6H_5$	397	m.p. 82–5°C
$(CH_3(C_6H_5)_2Si.CB_{10}H_{10}C.SiCH_3(C_6H_5)_2$	397	m.p. 138–40°C
$(CH_3)_2ClSi.CB_{10}H_{10}C.Si(CH_3)_2Cl$	393, 394	b.p. 108–10°C at 1 torr
$CH_3Cl_2Si.CB_{10}H_{10}C.SiCH_3Cl_2$	393	
$(C_6H_5)_2ClSi.CB_{10}H_{10}C.Si(C_6H_5)_2Cl$	393, 397	m.p. 121–2°C
$(CH_3)_2HOSi.CB_{10}H_{10}C.Si(CH_3)_2OH$	393	
$CH_3(HO)_2Si.CB_{10}H_{10}C.SiCH_3(OH)_2$	393	
$(C_6H_5)_2HOSi.CB_{10}H_{10}C.Si(C_6H_5)_2OH$	393	
$(CH_3)_2CH_3OSi.CB_{10}H_{10}C.Si(CH_3)_2OCH_3$	393–4	
$(C_6H_5)_2CH_3OSi.CB_{10}H_{10}C.Si(C_6H_5)_2OCH_3$	393	
$(CH_3)_2H_2NSi.CB_{10}H_{10}C.Si(CH_3)_2NH_2$	393	
$(CH_3)_2ClSi.O.(CH_3)_2Si.CB_{10}H_{10}C.Si(CH_3)_2.O.Si(CH_3)_2Cl$	394	b.p. 128°C at 0·08 torr

(j) *C*-germanium and *C*-tin Derivatives

Formula	Preparation references	Properties and references
$Cl_3Ge.CB_{10}H_{10}C.GeCl_3$	398	
$(CH_3)_2ClGe.CB_{10}H_{10}C.Ge(CH_3)_2Cl$	398	m.p. 59–61°C
$HCB_{10}H_{10}C.Sn(C_6H_5)_2Cl$	398	m.p. 72–3°C
$(CH_3)_3Sn.CB_{10}H_{10}C.Sn(CH_3)_3$	455	m.p. 68–9°C
$(C_4H_9)_3Sn.CB_{10}H_{10}C.Sn(C_4H_9)_3$	455	b.p. 134–5°C at 0·004 torr, n_D^{25} 1·5314
$(C_6H_5)_3Sn.CB_{10}H_{10}C.Sn(C_6H_5)_3$	455	m.p. 192°C
$(C_6H_5)_2ClSn.CB_{10}H_{10}C.Sn(C_6H_5)_2Cl$	455	
$(CH_3.CB_{10}H_{10}C—)_2Sn(CH_3)_2$	455	m.p. 107–8°C
$(CH_3.CB_{10}H_{10}C—)_2Sn(C_6H_5)_2$	455	m.p. 114–15°C
$(C_6H_5.CB_{10}H_{10}C—)_2Sn(CH_3)_2$	455	m.p. 142–3°C

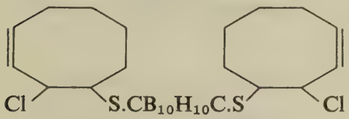
(k) *C*-phosphorus Derivatives

Formula	Preparation references	Properties and references
$(C_6H_5)_2P.CB_{10}H_{10}C.P(C_6H_5)_2$	456	m.p. 101°C
$C_6H_5ClP.CB_{10}H_{10}C.PC_6H_5Cl$	456	b.p. 229°C at 0·35 torr, n_D^{26} 1·6522
$C_6H_5.CH_3OP.CB_{10}H_{10}C.PC_6H_5OCH_3$	456	m.p. 112–14°C
$CH_3(CH_3)_2NP.CB_{10}H_{10}C.PCH_3.N(CH_3)_2$	456	m.p. 73–5°C
$C_6H_5.(CH_3)_2NP.CB_{10}H_{10}C.PC_6H_5.N(CH_3)_2$	456	m.p. 100–2°C
$Cl_2P.CB_{10}H_{10}C.PCl_2$	456	b.p. 119°C at 0·3 torr, n_D^{22} 1·6183
$(CH_3O)_2P.CB_{10}H_{10}C.P(OCH_3)_2$	456	n_D^{26} 1·5420
$(—CB_{10}H_{10}C.P[N(CH_3)_2]_2)_2PCl$	456	m.p. 90–4°C

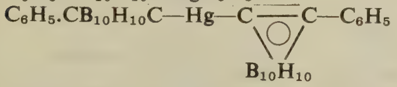
(l) *C*-sulphur Derivatives

Formula	Preparation references	Properties and references
$C_6H_5.CB_{10}H_{10}C.CSNC_6H_5$	371	m.p. 136–7°C
$HS.CB_{10}H_{10}C.SH$	409	m.p. 164–5°C
$C_2H_5S.CB_{10}H_{10}C.SC_2H_5$	409	b.p. 114°C at 0·1 torr
$p\text{-}CH_3.C_6H_4—S—CB_{10}H_{10}C—S—C_6H_4.CH_3\text{-}p$	409	m.p. 131–2°C

Table XXIX.—continued

Formula	Preparation references	Properties and references
$ClS.CB_{10}H_{10}C.SCl$	412, 454, 490	b.p. 97–8°C at 0·17 torr, n_D^{25} 1·6172
2-Cl-*cyclo*-C_6H_{10}—$S.CB_{10}H_{10}C.S$—*cyclo*-C_6H_{10}—Cl-2	412	
	412	m.p. 149–51°C
$C_2H_5OS.CB_{10}H_{10}C.SOC_2H_5$	412	b.p. 114–16°C at 0·15 torr, n_D^{25} 1·5521
$H_2NS.CB_{10}H_{10}C.SNH_2$	412	b.p. 120–3°C at 0·15 torr, n_D^{25} 1·6296
$NCS.CB_{10}H_{10}C.SCN$	412	m.p. 68–9°C
$ClO_2S.CB_{10}H_{10}C.SO_2Cl$	412, 454, 490	m.p. 62–3°C

(m) *C*-metal Derivatives

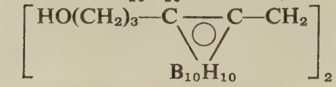
Formula	Preparation references	Properties and references
$CH_3.CB_{10}H_{10}C.HgCH_3$	386	m.p. 123–4°C
$CH_3.CB_{10}H_{10}C.HgCl$	386	m.p. 251–2°C
$CH_3.CB_{10}H_{10}C.HgBr$	386	m.p. 233–5°C
$CH_3.CB_{10}H_{10}C.HgCl$, (*o*-phenanthroline)	390	m.p. >280°C
$CH_3.CB_{10}H_{10}C.HgBr$, (*o*-phenanthroline)	390	m.p. 290–1°C decomp.
$C_6H_5.CB_{10}H_{10}C.HgCH_3$	386	m.p. 140–1°C
$C_6H_5.CB_{10}H_{10}C.HgC_6H_5$	386	m.p. 138–40°C
 $C_6H_5.CB_{10}H_{10}C—Hg—\underset{B_{10}H_{10}}{C—C}—C_6H_5$	386	m.p. 159–60°C
$C_6H_5.CB_{10}H_{10}C.HgCl$	386	m.p. 210–11°C
$C_6H_5.CB_{10}H_{10}C.HgBr$	386	m.p. 212–14°C
$CH_3.Hg.CB_{10}H_{10}C.HgCH_3$	386	m.p. 235–7°C
$BrHg.CB_{10}H_{10}C.HgBr$	386	m.p. 314–16°C
$(HCB_{10}H_{10}C—)_2Hg$	391	m.p. >400°C, polarography (391)
$(CH_3.CB_{10}H_{10}C—)_2Hg$	386, 391	m.p. 191–2°C, polarography (391)
$(C_6H_5.CB_{10}H_{10}C—)_2Hg$	386, 391	m.p. 179–80°C, polarography (391)
$(CH_3.CB_{10}H_{10}C—)_2Hg$, (*o*-phenanthroline)	390	m.p. >280°C decomp.
$(H.CB_{10}H_9ClC—)_2Hg$	391	m.p. 243–4°C, polarography (391)
$(CH_3CB_{10}H_{10}C—)—Pt[P(C_2H_5)_3]_2$	414	m.p. 100–1°C

(n) Difunctional Derivatives (see also Table XXVIII, 1:7-$C_2B_{10}H_{12}$ derivatives of 1:2-$C_2B_{10}H_{12}$, p. 538)

Formula	Preparation references	Properties and references
$H.CB_{10}H_{10}C—CB_{10}H_{10}C.H$	268, 453	m.p. 270–1°C, i.r. (282)
$CH_3.CB_{10}H_{10}C—(CH_2)_3—CB_{10}H_{10}C.CH_3$	371	m.p. 288–90°C
$(C_6H_5.CB_{10}H_{10}C—)_2CHOH$	373	m.p. 126–8°C
$(C_6H_5.CB_{10}H_{10}C—)_2CO$	373	m.p. 144–5°C
$C_6H_5.CB_{10}H_{10}C—COCH_2CHC_6H_5—CB_{10}H_{10}C.C_6H_5$	371	m.p. 91–2°C
$H.CB_{10}H_{10}C—C_6H_4$-*p*-N=N—C_6H_4-*p*-$CB_{10}H_{10}C.H$	324	m.p. 247–8°C

Table XXIX.—continued

(o) Polymeric Derivatives

Formula	Preparation references	Properties and references
$\mathrm{ClCO({-}CB_{10}H_{10}C{-}CO{-})_3Cl}$	376	b.p. 67°C at 0·1 torr, n_D^{25} 1·5443
$\mathrm{ClCO({-}CB_{10}H_{10}C{-}CO{-})_5Cl}$	376	m.p. 138–43°C
$\mathrm{HOOC.CB_{10}H_{10}C.COOH}$ +  $\left[\mathrm{HO(CH_2)_3{-}\underset{B_{10}H_{10}}{C{-}C}{-}CH_2}\right]_2$ O copolymer	474	Mol. wt. 1730 (474)
$\mathrm{[{-}CB_{10}H_{10}C{-}Si(CH_3)_2{-}]_n}$	459	m.p. 115–20°C, Mol. wt. 7400 (459)
$\mathrm{[{-}Si(CH_3)_2{-}CB_{10}H_{10}C{-}Si(CH_3)_2O{-}]_n}$	394	m.p. 233–40°C, Mol. wt. 16,500 (394), i.r. (394)
$\mathrm{\{{-}Si(CH_3)_2{-}CB_{10}H_{10}C{-}[Si(CH_3)_2O]_2{-}\}_n}$	394	
$\mathrm{\{{-}Si(CH_3)_2{-}CB_{10}H_{10}C{-}[Si(CH_3)_2O]_3{-}\}_n}$	394	
$\mathrm{\{{-}Si(CH_3)_2{-}CB_{10}H_{10}C{-}[Si(CH_3)_2O]_4{-}\}_n}$	394	
$\mathrm{[{-}CB_{10}H_{10}C{-}Ge(CH_3)_2{-}]_n}$	398, 457	Mol. wt. 1755 (398, 457)
$\mathrm{[{-}CB_{10}H_{10}C{-}Ge(C_6H_5)_2{-}]_n}$	457, 459	m.p. 92–5°C, Mol. wt. 1800 (457, 459)
$\mathrm{[{-}Ge(CH_3)_2{-}CB_{10}H_{10}C{-}Ge(CH_3)_2{-}NH{-}]_n}$	457	
$\mathrm{[{-}CB_{10}H_{10}C{-}Ge(CH_3)_2{-}]_n}$ + $\mathrm{[{-}CB_{10}H_{10}C{-}Sn(CH_3)_2{-}]_m}$ copolymer	398	m.p. 350–5°C
$\mathrm{[{-}CB_{10}H_{10}C{-}Sn(CH_3)_2{-}]_n}$	398, 457	m.p. 217–21°C, Mol. wt. 2560 (398, 457)
$\mathrm{[{-}CB_{10}H_{10}C{-}Sn(C_6H_5)_2{-}]_n}$	398, 457–9	m.p. 240–3°C, Mol. wt. 2400, 5000 (398, 459)
$\mathrm{[{-}CB_{10}H_9BrC{-}Sn(CH_3)_2{-}]_n}$	398	m.p. 380–3°C
$\mathrm{[{-}CB_{10}H_{10}C{-}Sn(CH_3)_2{-}]_n}$ + $\mathrm{[{-}1{:}12\text{-}CB_{10}H_{10}C{-}Sn(CH_3)_2{-}]_m}$ copolymer	398	m.p. 370–5°C
$\mathrm{({-}CB_{10}H_{10}C{-}PC_6H_5{-})_n}$	459	m.p. <200°C decomp.
$\mathrm{({-}CB_{10}H_{10}C{-}PCl{-})_n}$	401, 456	m.p. 120–35°C
$\mathrm{({-}CB_{10}H_{10}C{-}S{-})_n}$	412, 454, 490	m.p. 219–20°C, Mol. wt. 5400 (412)
$\mathrm{({-}S{-}CB_{10}H_{10}C{-}S{-})_n}$	412, 454, 490	m.p. 307–10°C, Mol. wt. 1770 (412)
$\mathrm{({-}S{-}CB_{10}H_{10}C{-}SO{-})_n}$	412	m.p. 281–3°C, Mol. wt. 2585 (412)

(p) *B*-fluorine Derivatives

Formula	Preparation references	Properties and references
$\mathrm{2\text{-}H.CB_{10}H_9FC.H}$	9, 432, 461	
$\mathrm{4\text{-}H.CB_{10}H_9FC.H}$	9, 432, 461	
$\mathrm{5\text{-}H.CB_{10}H_9FC.H}$	461	
$\mathrm{9\text{-}H.CB_{10}H_9FC.H}$	461	
$\mathrm{H.CB_{10}F_{10}C.H}$	428, 431	m.p. 240–2°C
$\mathrm{F.CB_{10}F_{10}C.F}$	428, 431	

(q) *B*-chlorine Derivatives

Formula	Preparation references	Properties and references
$\mathrm{2\text{-}H.CB_{10}H_9ClC.H}$	461	
$\mathrm{4\text{-}H.CB_{10}H_9ClC.H}$	461, 463	
$\mathrm{5\text{-}H.CB_{10}H_9ClC.H}$	461	

Table XXIX.—continued

Formula	Preparation references	Properties and references
$\mathrm{9\text{-}H.CB_{10}H_9ClC.H}$	429, 447, 461, 463	m.p. 218–19°C, ^{35}Cl n.q.r. (416), μ 14·1 × 10^{-30} C m (4·22 D) (293, 451)
$\mathrm{H.CB_{10}H_9ClC.H}$ (isomer a)	447, 464–5	m.p. 190–1°C
$\mathrm{H.CB_{10}H_9ClC.H}$ (isomer b)	304, 447, 465	m.p. 216°C
$\mathrm{9{:}10\text{-}H.CB_{10}H_8Cl_2C.H}$	304, 429, 465	m.p. 221–2°C, ^{35}Cl n.q.r. (416), μ 17·9 × 10^{-30} C m (5·37 D) (293, 451)
$\mathrm{H.CB_{10}H_8Cl_2C.H}$ (isomer a)	447, 465	m.p. 132–4°C
$\mathrm{H.CB_{10}H_8Cl_2C.H}$ (isomer b)	465	m.p. 187–8°C
$\mathrm{H.CB_{10}H_7Cl_3C.H}$ (isomer a)	447	m.p. 175–6°C
$\mathrm{H.CB_{10}H_7Cl_3C.H}$ (isomer b)	451	m.p. 253–4°C, ^{35}Cl n.q.r. (416), μ 19·5 × 10^{-30} C m (5·86 D) (293, 451)
$\mathrm{H.CB_{10}H_6Cl_4C.H}$	447	m.p. 280–1°C, μ 20·9 × 10^{-30} C m (6·26 D) (293, 451)
$\mathrm{H.CB_{10}Cl_{10}C.H}$	241, 304, 444, 449	m.p. 235°C, i.r. (304), ^{1}H n.m.r. (241), ^{11}B n.m.r. (241), *X*-ray (271), ^{35}Cl n.q.r. (416), μ 14·6 × 10^{-30} C m (4·39 D) (293, 451), pK_a 9·19 (444)
$\mathrm{Cl.CB_{10}Cl_{10}C.Cl}$	360	m.p. 443°C, i.r. (360), ^{11}B n.m.r. (360)
$\mathrm{9{:}10\text{-}CH_3.CB_{10}H_8Cl_2C.H}$	416	m.p. 154–5°C, ^{35}Cl n.q.r. (416)
$\mathrm{CH_3.CB_{10}Cl_{10}C.CH_3}$	360	^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
$\mathrm{C_2H_5.CB_{10}Cl_{10}C.C_2H_5}$	360	^{1}H n.m.r. (360), ^{11}B n.m.r. (360)
$\mathrm{H.CB_{10}Cl_8Br_2C.H}$	363, 427	m.p. 232–4°C

(r) *B*-bromine Derivatives

Formula	Preparation references	Properties and references
$\mathrm{2\text{-}H.CB_{10}H_9BrC.H}$	466	
$\mathrm{4\text{-}H.CB_{10}H_9BrC.H}$	466	
$\mathrm{5\text{-}H.CB_{10}H_9BrC.H}$	466	
$\mathrm{9\text{-}H.CB_{10}H_9BrC.H}$	304, 363, 418, 447, 465–6	m.p. 174–5°C, i.r. (282), μ 14·1 × 10^{-30} C m (4·24 D) (293, 451)
$\mathrm{H.CB_{10}H_9BrC.H}$	447, 465	m.p. 153–4°C
$\mathrm{9{:}10\text{-}H.CB_{10}H_8Br_2C.H}$	304, 363, 418, 427	m.p. 189–90°C, i.r. (282), *X*-ray (272), μ 17·1–18·0 × 10^{-30} C m (5·14–5·40 D) (291, 293, 451)
$\mathrm{H.CB_{10}H_8Br_2C.H}$ (isomer a)	447, 464	m.p. 81–2°C
$\mathrm{H.CB_{10}H_8Br_2C.H}$ (isomer b)	447, 464	m.p. 142–3°C
$\mathrm{H.CB_{10}H_7Br_3C.H}$ (isomer a)	304, 363	m.p. 274–6°C, i.r. (282)
$\mathrm{H.CB_{10}H_7Br_3C.H}$ (isomer b)	447	m.p. 135–6°C
$\mathrm{H.CB_{10}H_7Br_3C.H}$ (isomer c)	451	m.p. 221–2°C
$\mathrm{H.CB_{10}H_7Br_3C.H}$ (isomer d)	451	m.p. 188–9°C
$\mathrm{H.CB_{10}H_6Br_4C.H}$	429, 447, 465	m.p. 324–5°C, i.r. (282), μ 21·0 × 10^{-30} C m (6·29 D) (293, 451)
$\mathrm{H.CB_{10}H_4Br_6C.H}$	429	m.p. 314–15°C, i.r. (282)
$\mathrm{H.CB_{10}H_8Br_2C.CH_3}$	363	m.p. 113–14°C
$\mathrm{H.CB_{10}Cl_8Br_2C.H}$	363, 427	m.p. 232–4°C
$\mathrm{(—CB_{10}H_9BrC—PCl—CB_{10}H_9BrC—POCH_3—)_3}$	456	m.p. 115–20°C

Table XXIX.—continued

(s) *B*-iodine Derivatives

Formula	Preparation references	Properties and references
$9\text{-}H.CB_{10}H_9IC.H$	304, 418, 429	m.p. 111–12°C, i.r. (282), *X*-ray (273), μ 14·0 × 10^{-30} C m (4·20 D) (293, 451)
$9\text{-}H.CB_{10}H_9{}^{131}IC.H$	441	
$9{:}10\text{-}H.CB_{10}H_8I_2C.H$	304, 418, 429, 449	m.p. 188–9°C, μ 18·1 × 10^{-30} C m (5·43 D) (293, 451)
$9{:}10\text{-}CB_{10}H_8{}^{131}I_2C.H$	441	

(t) Miscellaneous *B*-substituted Derivatives

Formula	Preparation references	Properties and references
$9\text{-}H.CB_{10}H_9C.H$ | $9\text{-}H.CB_{10}H_9C.H$	442	m.p. 182–3°C
$2\text{-}H.CB_{10}H_9N(C_6H_5)_2.C.H$	432, 435	
$4\text{-}H.CB_{10}H_9N(C_6H_5)_2.C.H$	435	

Table XXX.—Closo-1:12-*dicarbadodecaborane*(12) *Derivatives*

Formula	Preparation references	Properties and references
$1{:}12\text{-}B_{10}H_{10}C_2HLi$	276	
$1{:}12\text{-}B_{10}H_{10}C_2Li_2$	276	
$1{:}12\text{-}B_{10}H_{10}C_2H.COOH$	276	m.p. 173–4°C, pK_a 3·64 in 50% EtOH
$1{:}12\text{-}B_{10}H_{10}C_2(COOH)_2$	276	m.p. 356–7°C
$1{:}12\text{-}B_{10}H_{10}C_2(SH)_2$	412	m.p. 157–8°C
$1{:}12\text{-}B_{10}H_{10}C_2(SCl)_2$	412	m.p. 71–3°C
$1{:}12\text{-}B_{10}H_{10}C_2(SO_2Cl)_2$	412	m.p. 181–3°C
$1{:}12\text{-}B_{10}H_9FC_2H_2$	461	
$1{:}12\text{-}B_{10}F_{10}C_2H_2$	428, 431	m.p. 222–4°C
$1{:}12\text{-}C_2H_2\text{-}2\text{-}B_{10}H_9Cl$	306, 461	m.p. 191–2°C, μ 5·57 × 10^{-30} C m (1·67 D) (307), ^{35}Cl n.q.r. (468)
$1{:}12\text{-}C_2H_2\text{-}2{:}9\text{-}B_{10}H_8Cl_2$	307	m.p. 148–9°C, μ 5·58 × 10^{-30} C m (1·69 D) (307)
$1{:}12\text{-}B_{10}HCl_9C_2H_2$	306	
$1{:}12\text{-}B_{10}Cl_{10}C_2H_2$	306	
$1{:}12\text{-}B_{10}H_8Br_2C_2H_2$	306	
$1{:}12\text{-}B_{10}H_8I_2C_2H_2$	306	
$[\text{—}1{:}12\text{-}CB_{10}H_{10}C\text{—}Ge(CH_3)_2\text{—}]_n$	398	m.p. 460–80°C, Mol. wt. 1470 (398)
$[\text{—}1{:}12\text{-}CB_{10}H_{10}C\text{—}Sn(CH_3)_2\text{—}]_n$	398	m.p. 365–75°C, Mol. wt. 6050 (398)
$[\text{—}1{:}12\text{-}CB_{10}H_{10}C\text{—}Sn(C_6H_5)_2\text{—}]_n$	398	m.p. 404–12°C, Mol. wt. 4780 (398)
$[\text{—}1{:}12\text{-}CB_{10}H_{10}C\text{—}Sn(CH_3)_2\text{—}]_m$ $+ [\text{—}1{:}7\text{-}CB_{10}H_{10}C\text{—}Sn(CH_3)_2\text{—}]_n$ copolymer	398	m.p. 320–5°C
$(\text{—}1{:}12\text{-}CB_{10}H_{10}C\text{—}S\text{—})_n$	412	m.p. > 420°C

Table XXXI.—Metal Sandwich Complexes of the Isomeric nido-*undecahydrodicarbaundecaborate,* $C_2B_9H_{11}^{2-}$ *Ions in which the Metal Ion occupies the* 3-*position in all cases*

Formula	Preparation references	Properties and references
$(1{:}2\text{-}C_2B_9H_{11})_2Cr^-$	179	i.r. (179), u.v. (179), μ_{eff} 35·2 × 10^{-24} A m^2 (3·85 B.M.)
$\pi\text{-}C_5H_5\text{—}Cr\text{—}1{:}2\text{-}C_2B_9H_{11}$	179	m.p. 248–9°C, i.r. (179), u.v. (179)
$1{:}2\text{-}C_2B_9H_{11}Cr(CO)_3^{2-}$	503	i.r. (503), ^{11}B n.m.r. (503)
$(1{:}2\text{-}C_2HCH_3B_9H_9)_2Cr^-$	179	i.r. (179), u.v. (179)
$\pi\text{-}C_5H_5\text{-}Cr\text{-}1{:}2\text{-}C_2HCH_3B_9H_9$	179	m.p. 219–20°C, i.r. (179), u.v. (179)
$[1{:}2\text{-}C_2(CH_3)_2B_9H_9]_2Cr^-$	179	i.r. (179), u.v. (179)
$\pi\text{-}C_5H_5\text{—}Cr\text{-}1{:}2\text{-}C_2(CH_3)_2B_9H_9$	179	m.p. 261–2°C, i.r. (179), u.v. (179)
$[1{:}2\text{-}C_2HC_6H_5B_9H_9]_2Cr^-$	179	i.r. (179), u.v. (179)
$\pi\text{-}C_5H_5\text{—}Cr\text{-}1{:}2\text{-}C_2HC_6H_5B_9H_9$	179	m.p. 208–9°C, i.r. (179), u.v. (179)
$1{:}2\text{-}C_2B_9H_{11}Mo(CO)_3^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}Mo(CO)_3H^-$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}Mo(CO)_3CH_3^-$	178	i.r. (178)
$1{:}2\text{-}C_2(CH_3)_2B_9H_9Mo(CO)_3^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}Mo(CO)_3Mo(CO)_5^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}Mo(CO)_3W(CO)_5^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}W(CO)_3^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}W(CO)_3CH_3^-$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}W(CO)_3W(CO)_5^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}W(CO)_3Mo(CO)_5^{2-}$	178	i.r. (178)
$1{:}2\text{-}C_2B_9H_{11}Mn(CO)_3^-$	178, 499	i.r. (178), u.v. (178, 499)
$1{:}2\text{-}C_2B_9H_{11}Re(CO)_3^-$	178, 499	i.r. (178), u.v. (178, 499), *X*-ray (514)
$(1{:}2\text{-}C_2B_9H_{11})_2Fe^{2-}$	176, 178	^{1}H n.m.r. (178), u.v. (176, 178)
$(1{:}2\text{-}C_2B_9H_{11})_2Fe^-$	176, 178, 290, 500	i.r. (178, 290), ^{11}B n.m.r. (176, 178), u.v. (178, 290), μ_{eff} 19·4 × 10^{-24} A m^2 (2·10 B.M.) (178), e.s.r. (519), Mössbauer spectrum (517)
$\pi\text{-}C_5H_5\text{—}Fe\text{—}1{:}2\text{-}C_2B_9H_{11}^-$	178, 501	i.r. (178, 501), ^{1}H n.m.r. (178), ^{11}B n.m.r. (501), u.v. (178)
$\pi\text{-}C_5H_5\text{—}Fe\text{—}1{:}2\text{-}C_2B_9H_{11}$	178, 501	m.p. 181–2°C, i.r. (178, 501), ^{11}B n.m.r. (178, 501), u.v. (178), *X*-ray (502), e.s.r. (519), Mössbauer spectrum (517)
$(1{:}2\text{-}C_2B_9H_{11})_2Fe_2(CO)_4^{2-}$	503	i.r. (503), ^{11}B n.m.r. (503)
$[1{:}2\text{-}C_2(CH_3)_2B_9H_9]_2Fe^{2-}$	176, 178	^{1}H n.m.r. (176, 178), ^{11}B n.m.r. (176), u.v. (178)
$[1{:}2\text{-}C_2(CH_3)_2B_9H_9]_2Fe^-$	178	$(CH_3)_4N^+$ salt: m.p. 247–9°C, i.r. (178), ^{11}B n.m.r. (178), u.v. (178), μ_{eff} 18·5 × 10^{-24} A m^2 (1·99 B.M.) (178), e.s.r. (519)
$(1{:}2\text{-}C_2HC_6H_5B_9H_9)_2Fe^{2-}$	178	^{1}H n.m.r. (178), u.v. (178)
$(1{:}2\text{-}C_2HC_6H_5B_9H_9)_2Fe^-$	178	$(CH_3)_4N^+$ salt: m.p. > 300°C, i.r. (178), ^{11}B n.m.r. (178), u.v. (178), μ_{eff} 17·3 × 10^{-24} A m^2 (1·87 B.M.) (178), e.s.r. (519)
$(1{:}2\text{-}C_2B_9H_{11})_2Co^{2-}$	177	
$(1{:}2\text{-}C_2B_9H_{11})_2Co^-$	177–8, 290, 500	i.r. (178, 290), ^{1}H n.m.r. (178), ^{11}B n.m.r. (177), u.v. (177–8, 290), polarography (177), *X*-ray (516), Co^{59} n.q.r. (518)
$\pi\text{-}C_5H_5\text{—}Co\text{—}1{:}2\text{-}C_2B_9H_{11}$	177–8	i.r. (178), ^{1}H n.m.r. (177–8), ^{11}B n.m.r. (177, 178), u.v. (177–8), m.p. 246–8°C
$1{:}2\text{-}C_2B_9H_{11}Co(CO)_2^{2-}$	503	i.r. (503), ^{11}B n.m.r. (503)
$[1{:}2\text{-}C_2(CH_3)_2B_9H_9]_2Co^-$	177–8	$(CH_3)_4N^+$ salt: m.p. 273–5°C, i.r. (178), ^{1}H n.m.r. (178), u.v. (178), polarography (177)
$(1{:}2\text{-}C_2HC_6H_5B_9H_9)_2Co^-$	177–8	$(CH_3)_4N^+$ salt: m.p. 290–3°C, i.r. (178), ^{1}H n.m.r. (178), u.v. (178), polarography (177)

Table XXXI.—continued

Formula	Preparation references	Properties and references
$(6\text{-}C_6H_5\text{-}1{:}2\text{-}C_2B_9H_{10})_2Co^-$	433	$(CH_3)_4N^+$ salt: m.p. 275–7°C, ^1H n.m.r. (433)
$(8{:}9{:}12\text{-}Br_3\text{-}1{:}2\text{-}C_2B_9H_8)_2Co^-$	178	i.r. (178), ^1H n.m.r. (178), u.v. (178), *X*-ray (511)
$[(1{:}2\text{-}C_2B_9H_{11})Co]_2C_2B_8H_{10}$	504	^1H n.m.r. (504), ^{11}B n.m.r. (504), u.v. (504), *X*-ray (525)
$(1{:}2\text{-}C_2B_9H_{11})_2Ni^{2-}$	178	i.r. (178), u.v. (178), μ_{eff} $26{\cdot}8 \times 10^{-24}$ A m^2 (2·90 B.M.)
$(1{:}2\text{-}C_2B_9H_{11})_2Ni^-$	178, 500	i.r. (178), u.v. (178, 500), μ_{eff} $16{\cdot}4 \times 10^{-24}$ A m^2 (1·76 B.M.) (178)
$(1{:}2\text{-}C_2B_9H_{11})_2Ni$	178, 500	i.r. (178), u.v. (178, 500), polarography (506), m.p. 265°C decomp.
$\pi\text{-}C_5H_5\text{—}Ni\text{-}1{:}2\text{-}C_2B_9H_{11}$	506	u.v. (506), μ_{eff} $18{\cdot}5 \times 10^{-24}$ A m^2 (1·99 B.M.) (506), polarography (506)
$(1{:}2\text{-}C_2B_9H_{11})_2Pd^{2-}$	507	i.r. (507), ^{11}B n.m.r. (507), u.v. (507)
$(1{:}2\text{-}C_2B_9H_{11})_2Pd^-$	507	i.r. (507), u.v. (507)
$(1{:}2\text{-}C_2B_9H_{11})_2Pd$	507	i.r. (507), u.v. (507)
$[(C_6H_5)_4C_4]\text{-}Pd\text{-}1{:}2\text{-}C_2B_9H_{11}$	178, 505	i.r. (178), u.v. (178), m.p. 310°C decomp.
$[(C_6H_5)_4C_4]\text{-}Pd\text{-}1{:}2\text{-}C_2(CH_3)_2B_9H_9$	178, 505	i.r. (178), ^1H n.m.r. (505), ^{11}B n.m.r. (505), u.v. (178), *X*-ray (505)
$(1{:}2\text{-}C_2B_9H_{11})_2Cu^{2-}$	508	*X*-ray (513)
$(1{:}2\text{-}C_2B_9H_{11})_2Cu^-$	507	i.r. (507), ^{11}B n.m.r. (507), u.v. (507), *X*-ray (512)
$(1{:}2\text{-}C_2B_9H_{11})_2Ag^{3-}$	508	
$(1{:}2\text{-}C_2B_9H_{11})_2Au^{2-}$	507	i.r. (507), u.v. (507)
$(1{:}2\text{-}C_2B_9H_{11})_2Au^-$	507	i.r. (507), ^{11}B n.m.r. (507), u.v. (507)
$1{:}2\text{-}C_2B_9H_{11}BeO(C_2H_5)_2$	509–10	m.p. 120–1°C, ^1H n.m.r. (509)
$1{:}2\text{-}C_2B_9H_{11}BeN(CH_3)_3$	509	m.p. 221–3°C decomp., ^1H n.m.r. (509)
$(1{:}7\text{-}C_2B_9H_{11})_2Cr^-$	179	i.r. (179), u.v. (179)
$\pi\text{-}C_5H_5\text{—}Cr\text{-}1{:}7\text{-}C_2B_9H_{11}$	179	m.p. 217–18°C, i.r. (179), u.v. (179)
$(1{:}7\text{-}C_2B_9H_{11})_2Ni^-$	178	$(CH_3)_4N^+$ salt: m.p. >300°C, i.r. (178), u.v. (178), μ_{eff} $16{\cdot}2 \times 10^{-24}$ A m^2 (1·74 B.M.) (178)
$(1{:}7\text{-}C_2B_9H_{11})_2Ni$	178	i.r. (178), u.v. (178)

Table XXXII.—Transition-metal Complexes of the $CB_{10}H_{11}^{3-}$ *and* $CB_{10}H_{10}$, [*amine*]$^{2-}$ *Ions*

Formula	Preparation references	Properties and references
$(CB_{10}H_{11})_2Cr^{3-}$	160	
$(CB_{10}H_{11})_2Mn^{2-}$	160	
$(CB_{10}H_{11})_2Fe^{3-}$	161	
$(CB_{10}H_{11})_2Co^{3-}$	160, 161	
$(CB_{10}H_{11})_2Co^{2-}$	160	u.v. (161)
$(CB_{10}H_{11})_2Ni^{2-}$	160, 161, 520	
$(CB_{10}H_{10}.OH)_2Ni^{2-}$	160	
$(CB_{10}H_{10},NH_3)_2Fe^-$	160	
$(CB_{10}H_{10},NH_3)_2Ni$	520	m.p. >400°C, i.r. (520)
$CB_{10}H_{10}.NH_2CoCB_{10}H_{10},NH_3{}^{2-}$	160	
$(CB_{10}H_{10},NH_2C_2H_5)_2Co^-$	161	
$[CB_{10}H_{10},NH_2\text{-}n\text{-}C_3H_7]_2Ni$	161	
$[CB_{10}H_{10},NH(CH_3)_2]_2Ni$	160	

Table XXXIII.—Transition-metal Complexes of the Smaller Nido-*Carborane Anions*

Formula	Preparation references	Properties and references
$C_2B_6H_8Mn(CO)_3^-$	524	^{11}B n.m.r. (524), ^{1}H n.m.r. (524)
$C_2(CH_3)_2B_6H_6Mn(CO)_3^-$	523–4	^{11}B n.m.r. (523–4), ^{1}H n.m.r. (523–4), u.v. (523)
$C_2HC_6H_5B_6H_6Mn(CO)_3^-$	524	^{11}B n.m.r. (524), ^{1}H n.m.r. (524)
$[(2):1:6\text{-}C_2B_7H_9]_2Co^-$	163–4	$(CH_3)_4N^+$ salt: m.p. 240°C, i.r. (164), ^{11}B n.m.r. (163–4), ^{1}H n.m.r. (163–4), u.v. (163, 164)
$\pi\text{-}C_5H_5\text{-}Co\text{-}(2):1:6\text{-}C_2B_7H_9$	163–4	m.p. 158–9°C, i.r. (164), ^{11}B n.m.r. (163–4), ^{1}H n.m.r. (163–4), u.v. (163–4)
$\pi\text{-}C_5H_5\text{-}Co\text{-}(2):1:6\text{-}C_2H_2B_7H_5Br_2$	522	m.p. 129–30°C
$\pi\text{-}C_5H_5\text{-}Co\text{-}(2):1:6\text{-}C_2B_7H_8.COCH_3$	522	m.p. 162°C, ^{11}B n.m.r. (522), ^{1}H n.m.r. (522)
$[(2):1:10\text{-}C_2B_7H_9]_2Co^-$	164, 521	Cs^+ salt: m.p. 210°C, ^{11}B n.m.r. (164, 521), u.v. (164, 521)
$\pi\text{-}C_5H_5\text{-}Co\text{-}(2):1:10\text{-}C_2B_7H_9$	164, 521	m.p. 113°C, i.r. (164), u.v. (521), ^{11}B n.m.r. (164, 521), ^{1}H n.m.r. (164)
$[(2):6:7\text{-}C_2B_7H_9]_2Co^-$	164	Cs^+ salt: m.p. 235°C, i.r. (164), ^{11}B n.m.r. (164), ^{1}H n.m.r. (164), u.v. (164)
$[(3):1:2\text{-}C_2B_9H_{11}Co]_2C_2B_8H_{10}$	504	^{11}B n.m.r. (504), ^{1}H n.m.r. (504), u.v. (504), *X*-ray (525)
$C_3B_3H_5CH_3Mn(CO)_3$	526	^{11}B n.m.r. (526), ^{1}H n.m.r. (526)

Table XXXIV.—Hetero-Element-Substituted Carboranes and Derivatives

Formula	Preparation references	Properties and references
$1:2\text{-}C_2H_2\text{-}3\text{-}AlC_2H_5B_9H_9,2C_4H_8O$	530	m.p. 120°C decomp.
$C_2B_4H_6GaCH_3$	531	m.p. 34°C, ^{11}B n.m.r. (531), ^{1}H n.m.r. (531), m.s. (531)
$1:2\text{-}B_{10}H_{10}CHGeCH_3$	526	m.p. 216–17°C
$1:2\text{-}B_{10}H_{10}CHGe^-$	526	
$3\text{-}Sn\text{-}1:2\text{-}C_2B_9H_{11}$	533	i.r. (533), ^{1}H n.m.r. (533), ^{11}B n.m.r. (533)
$1:2\text{-}B_{10}H_{10}CHP$	535–6	m.p. 354°C, i.r. (536), ^{11}B n.m.r. (536), ^{1}H n.m.r. (536), u.v. (536)
$1:2\text{-}B_{10}H_9BrCHP$	536	m.p. 245°C, i.r. (536), ^{1}H n.m.r. (536)
$1:2\text{-}B_{10}H_8Br_2CHP$	536	m.p. 255–6°C, i.r. (536), ^{1}H n.m.r. (536)
$1:2\text{-}B_{10}H_7Br_3CHP$	535–6	m.p. 352–3°C, i.r. (536), ^{1}H n.m.r. (536)
$(3):1:2\text{-}B_9H_{10}CHPCH_3$	536–7	m.p. 108–9°C, i.r. (536), ^{1}H n.m.r. (536)
$(3):1:2\text{-}B_9H_{10}CHP^-$	536	^{1}H n.m.r. (536)
$(3):1:2\text{-}B_9H_{11}CHP,NC_5H_{10}$	536–7	m.p. 307–8°C, i.r. (536), ^{1}H n.m.r. (536)
$1:2\text{-}B_9H_{10}CHPCr(CO)_5^-$	538	i.r. (538), ^{1}H n.m.r. (538)
$1:2\text{-}B_9H_{10}CHPMo(CO)_5^-$	538	i.r. (538), ^{1}H n.m.r. (538)
$1:2\text{-}B_9H_{10}CHPW(CO)_5^-$	538	i.r. (538), ^{1}H n.m.r. (538), ^{31}P n.m.r. (538)
$(1:2\text{-}B_9H_9CHPCH_3)_2Fe$	537	
$1:7\text{-}B_{10}H_{10}CHP$	535–6	m.p. 325–7°C, i.r. (536), ^{11}B n.m.r. (536), ^{1}H n.m.r. (536), u.v. (536)
$1:7\text{-}B_{10}H_{10}CCH_3P$	535	
$1:7\text{-}B_{10}H_9BrCHP$	536	m.p. 226–8°C, i.r. (536)
$1:7\text{-}B_{10}H_8Br_2CHP$	536	m.p. 234–5°C, i.r. (536)
$(3):1:7\text{-}B_9H_{11}CHP$	536	m.p. 206–10°C, i.r. (536)
$(3):1:7\text{-}B_9H_{10}CHPCH_3$	536–7	m.p. 112–13°C, i.r. (536, 537), ^{11}B n.m.r. (536), ^{1}H n.m.r. (536)
$(3):1:7\text{-}B_9H_{10}CHP^-$	536	i.r. (536), ^{1}H n.m.r. (536)
$(3):1:7\text{-}B_9H_{11}CHP,NC_5H_{10}$	536–7	m.p. 296–7°C, i.r. (536)
$1:7\text{-}B_9H_{10}CHPCr(CO)_5^-$	538	i.r. (538), ^{1}H n.m.r. (538)

Table XXXIV.—continued

Formula	Preparation references	Properties and references
$1{:}7\text{-}B_9H_{10}CHPMo(CO)_5^-$	538	i.r. (538), ^1H n.m.r. (538)
$1{:}7\text{-}B_9H_{10}CHPW(CO)_5^-$	538	i.r. (538), ^1H n.m.r. (538)
$1{:}7\text{-}B_9H_9CHPCH_3Mn(CO)_3$	537	
$(1{:}7\text{-}B_9H_9CHPCH_3)_2Fe$ (isomer a)	537	m.p. 239–41°C, *X*-ray (537), optical resolution (537)
$(1{:}7\text{-}B_9H_9CHPCH_3)_2Fe$ (isomer b)	537	m.p. 233–4°C
$\pi\text{-}C_5H_5\text{-}Fe\text{-}1{:}7\text{-}B_9H_9CHPCH_3$	537	
$(1{:}7\text{-}B_9H_9CHPCH_3)_2Co$ (isomer a)	537	m.p. 278–9°C
$(1{:}7\text{-}B_9H_9CHPCH_3)_2Co$ (isomer b)	537	m.p. 231–4°C
$[\pi\text{-}(3){:}1{:}7\text{-}B_9H_9CHP]_2Fe^{2-}$	537	
$[\pi\text{-}(3){:}1{:}7\text{-}B_9H_9CHP]_2Co^{2-}$	537	
$1{:}12\text{-}B_{10}H_{10}CHP$	536	m.p. 314–16°C, i.r. (536), ^1H n.m.r. (536)
$1{:}2\text{-}B_{10}H_{10}CHAs$	532	m.p. 399–400°C
$(3){:}1{:}2\text{-}B_9H_{10}CHAs^-$	532	
$(3){:}1{:}2\text{-}B_9H_9CHAs^{2-}$	532	
$1{:}2\text{-}B_9H_{10}CHAsMo(CO)_5^-$	538	i.r. (538), ^{11}B n.m.r. (538), ^1H n.m.r. (538)
$1{:}7\text{-}B_{10}H_{10}CHAs$	532	m.p. 351–2°C
$1{:}7\text{-}B_9H_{10}CHAsCr(CO)_5^-$	538	i.r. (538), ^1H n.m.r. (538)
$1{:}7\text{-}B_9H_{10}CHAsMo(CO)_5^-$	538	i.r. (538), ^1H n.m.r. (538)
$1{:}7\text{-}B_9H_{10}CHAsW(CO)_5^-$	538	i.r. (538), ^1H n.m.r. (538)
$1{:}12\text{-}B_{10}H_{10}CHAs$	532	m.p. 335–7°C, ^{11}B n.m.r. (532)
$1{:}2\text{-}B_{10}H_{10}CHSb$	532	
$(3){:}1{:}2\text{-}B_9H_{10}CHSb^-$	532	
$(3){:}1{:}2\text{-}B_9H_9CHSb^{2-}$	532	
$1{:}7\text{-}B_{10}H_{10}CHSb$	532	m.p. 404–5°C

RECENT DEVELOPMENTS

The rapid development of carborane chemistry has been confirmed in the interval since the preparation of the original manuscript for this chapter. In this interval a substantial fraction of the total carborane literature has been published. Accordingly, a supplementary bibliography has been added. For the convenience of the reader, this has been classified and arranged in a similar fashion to the chapter as a whole and all titles have been included. This bibliography should be nearly comprehensive up to the end of 1973 and includes most work published in the first half of 1974.

Attention may be drawn to some of the more important recent developments. Grimes has written an authoritative book on the general subject[554] and very detailed N.M.R. data are now available.[553] A number of important review lectures were given at recent I.U.P.A.C. conferences.[574, 575, 797, 882, 953] Very accurate S.C.F. calculations are now available for some carboranes[563, 590] as are detailed studies of vibrational spectra.[602] Major improvements in the methods used to prepare the small *closo*-carboranes have occurred[591] and the exciting *closo*-carborane, $C_3B_5H_7$, which contains a bare carbon atom, has been reported.[598] Three new *nido*-carborane families have been discovered, namely $C_2B_7H_{11}$, $C_2B_8H_{12}$ and $C_2B_3H_7$.[623, 627] Several groups have reported sigma-bonded transition-metal derivatives of carboranes[918, 925, 954] and even lanthanide derivatives have been mentioned.[944] Hawthorne has reported two interesting developments in the chemistry of metallo-carboranes: some new isomers of a dicarbollide complex of Co(III) have been discovered[932], and $B_9C_2H_{12}$-$AlMe_2$ has been shown to be a fluxional molecule on the X-ray time scale.[944] Finally, we note the increased success of polymeric carboranes.[882]

The reader's attention is also directed to the revised nomenclature for carboranes, which has been clearly set out in an I.U.P.A.C. booklet.[576]

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